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VOL. V No. 5

SOIL SCIENCE

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PUBLISHED MONTHLY BY
WILLIAMS & WILKINS COMPANY
BALTIMORE, MD., U. S. A.

THE CAMBRIDGE UNIVERSITY PRESS
FETTER LANE, LONDON, E. C.

Entered as second-class matter August 23, 1917, at the post office at Baltimore, Maryland, under the act of March 3, 1879.
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THE INVERSION OF CANE SUGAR BY SOILS AND ALLIED SUBSTANCES AND THE NATURE OF SOIL ACIDITY

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Received for publication March 25, 1918

By the earlier investigators the inversion of cane sugar was believed to be catalyzed by hydrogen ions and by no other non-organized substance. (Inversion by enzymes will not be considered in this paper.) Ostwald (67), Arrhenius (9), Palmaer (69), Ley (52), and others believed so implicitly that inversion could not be produced in any other way that, whenever discrepancies appeared in their results, they were attributed to side reactions taking place, or to physical disturbances in the system.[1] Thus were hydrogen ions detected, and hydrogen-ion concentration determined—by measuring the rate of inversion of sucrose (95). The majority of chemists today believe as did those earlier workers, though some would modify the hypothesis to include undissociated hydrogen as also having catalytic action in some cases.[2]

From time to time phenomena have been recorded which at first sight appeared to be instances of inversion where acid hydrogen was not present. But in these cases it was never conclusively proven that acid hydrogen was not present either at the start, or formed later through the decomposition of the sugar itself. Cane sugar is quite easily decomposed, and among the products of decomposition, substances of an acid character seem to predominate. Thus often conditions may be such that although no acid is present at the beginning of an experiment, it may later be formed, inversion then taking place (10, 99). Such cases are recognized by determining at intervals the amount of sugar inverted, when it is found that as time goes on, the sugar is inverted at a greater and greater rate. On the other hand, if the action were due only to acid present at the beginning, then the rate of inversion must fall off as the reaction proceeds, since according to the mass law, the amount of sugar acted upon at a given time must depend upon the amount present at that time to be acted upon. Rayman and Sulc and others (49, 76, 85) have found that pure water causes inversion at high temperatures; the rate is low at first but as the heating continues it becomes greater. The initial inversion is attributed to that slight quantity of hydrogen ion always present in water, and the increase in rate, to acid produced through the decomposition of the sugar.

[1] Hence arose the ideas of "active" and "inactive" sugar molecules, stimulation of the catalytic activity of hydrogen ions, increased rate of movement of hydrogen ions, internal friction in solutions, increase in the osmotic pressure of the sugar in solution, and so on.

[2] Acree (4) and Snethlage (86) believe that in the case of the stronger acids undissociated acid hydrogen is even more active in causing inversion of sugar than hydrogen ion. See also Lamble and Lewis (50) and Harned (39).

Inversion by metals and metallic powders has been observed by Rayman and Sulc (76), Lindet (53), and Plzak and Husek (73), but again we must conclude that the sugar is first decomposed, and it is the products of this decomposition that are effective (99). Inversion by sunlight (75), the electric current (66), ultraviolet light (15, 29), and radium (46) are to be explained in the same way.

The action of salts on sucrose has been carefully studied. As should be expected, if a salt hydrolyses in solution with the formation of acid hydrogen, then inversion must take place. Such has been found to be the case with cadmium, zinc, lead and aluminum nitrates (101), manganese, zinc, iron and aluminum sulfates, iron, manganese, lead, cadmium, and mercuric chlorides (57), chromium sulfate (103), aluminum and copper chlorides, cadmium, copper and nickel sulfates (45). Salts of bases with acids of equal strength, or of strong bases with weak acids, do not invert.[3]

Geerligs (33) made the interesting observation that while invert sugar exhibited no action on sucrose when alone and neither did such neutral salts as the chlorides of potassium, sodium, lithium, calcium, strontium, barium and magnesium, yet if invert sugar was present in solution together with any of these salts, hydrolysis of the sucrose did take place. It was explained by postulating that through hydrolysis of the salt, and a combination of the basic part with the monose sugar, the acid was left free to exert the characteristic inverting effect. The following equation was given to explain this:

$$\underset{\text{salt}}{MA} + \underset{\text{water}}{HOH} + \underset{\text{glucose}}{C_6H_{12}O_6} = \underset{\text{basic glucose compound}}{MOH\ C_6H_{12}O_6} + \underset{\text{ionized acid}}{HA}$$

Contradictory results, however, were obtained by Deerr (28).

The literature on the subject of sucrose inversion is voluminous, but it has never been proven that this reaction can be effected in any other chemical way than through the presence of acid.

INVERSION OF CANE SUGAR BY SOILS

That soils will cause inversion of cane sugar has already been shown by Tacke and Süchting (94), and by Hanley (37). It seemed to these investigators that organic matter was the principal factor in producing the effect. The following experiments will show, however, that inversion must be attributed in large measure to the mineral portion as well.

Experiment 1

Here recorded are a number of soils of all types, which have significant inverting action.

To 50 cc. of a 5 per cent cane sugar solution 5 gm. of soil were added. The mixture was heated 1½ hours on a water bath at a temperature of 83° to 85°C.

[3] The action of some neutral salts in increasing the inverting power of strong acids has been of considerable interest, but will not be taken up here. See especially Spohr (89), also Acree (4) and Snethlage (86), and many others.

The quantity of invert sugar was determined in an aliquot of the filtrate by Cole's method (25), and reported in terms of grams of sucrose inverted. In another portion of the filtrate, the hydrogen-ion concentration was determined by the colorimetric method perfected by Sörensen (88, 102). The results for hydrogen-ion concentration are given in the same terms as used by Sörensen: $P(H)$, as the logarithm (base 10) of the normality with respect to hydrogen ions, the minus sign being understood. For instance, a $P(H)$ of 6.1 refers to a hydrogen-ion concentration of $10^{-6.1}$ normal. Soils are arranged in order of decreasing powers of inversion:

SOIL	SUGAR INVERTED PER 50 CC.	P (H)
	gram	
Japanese, 14	0.6179	7.07
Japanese, 11	0.1850	6.98
Japanese, 13	0.1360	7.08
Japanese, 10	0.1248	7.13
Japanese, 8	0.1197	7.14
New York, P2	0.1132	7.08
New York, 00	0.1054	7.07
New York, Turkey Hill, 0	0.0986	7.08
New York, 720	0.0980	7.08
New York, 729	0.0935	7.08
Japanese, 5	0.0890	6.98
Japanese, 7	0.0872	7.08
New York, 16207	0.0852	7.13
Japanese, 6	0.0811	6.98
New York, Dutchess Silt Loam, Orange Co., 1	0.0722	7.06
New York, P3	0.0680	7.14
New York, 1691	0.0644	7.06
New York, 1	0.0554	7.06
New York, Roberts 1	0.0545	7.14
New York, 724	0.0510	7.14
New York, Vergennes Clay, Washington County	0.0510	6.98
New York, Dutchess Silt Loam, 2	0.0482	6.98
New York, Cornell Wood Lot	0.0476	7.09
Japanese, 4	0.0476	7.13
New York, "Alfalfa"	0.0452	7.15
New York, 2109	0.0456	7.14
New York, 732	0.0442	7.14
New York, Vergennes Clay, Jefferson County	0.0421	7.14
New York, "Potato"	0.0380	7.08
New York, Turkey Hill, V	0.0300	7.14
New York, Ontario Loam, Oneida County	0.0244	7.14
New York, P1	0.0228	7.14
New York, Ontario Loam, Monroe County	0.0210	7.14
New York, 1613	0.0224	7.14
New York, 11	0.0182	7.14
New York, 6 (alkaline)	0.0000	7.35
Muck, 1713	0.0277	
Muck, 1712	0.0252	
Muck, 175	0.0210	
Muck, 1711	0.0193	

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Muck, 1713	0.0277	
Muck, 1712	0.0252	
Muck, 175	0.0210	
Muck, 1711	0.0193	

A solution of sugar made up to 5 per cent such as was used in this experiment, was found to contain 0.0026 gm. of invert sugar per 50 cc., and to have $P(H)$ of 7.07. The same solution heated for 3 hours under the conditions observed above, was then found to have 0.0036 gm. of invert sugar per 50 cc., and $P(H)$ of 7.06. It has already been mentioned that water had been found by others to have some decomposing action on sucrose; however, it is seen, that under the conditions of these experiments, this action is so small that it may be generally neglected. As a further precaution, water extracts of several soils were titrated as in Cole's procedure, to find whether or not some of the reducing power might be due to something dissolved from the soils: the mucks were found to yield slightly reducing extracts, but the mineral soils showed either none at all or very little, indeed. This factor may also be neglected, except, perhaps, where the total inversion is found to be exceedingly slight.

THE CHARACTER OF THE SOIL EXTRACTS

Bearing in mind that a solution of absolute neutrality has a hydrogen-ion concentration of $10^{-7.07}$ normal, it may be seen from the above experiment that soils can exhibit significant inverting power while their sugar extracts are only slightly acid, and in most cases neutral or alkaline. This would seem to indicate that inversion is principally a property of the solid phase—that there cannot be enough acid in solution to account for all. However, attention was given to the possibility of catalytic action being due to something in the solution phase.

In considering this possibility, there are two conditions under which it might be found to hold. First, there may be some water-soluble acid in these soils. (Hanley found frequently that the water extracts of his soils had inverting power.) Second, there may be some soil acids that are not soluble in water, yet are soluble in cane sugar solution. (There are many known cases of substances being more soluble in sugar solution than in water (100).)

If water-soluble acid is present in the soils, then water extracts should exhibit inverting action.

Experiment 2

Ten-gram portions of some of the most acid New York soils were extracted with 50 cc. of distilled water, allowing the water to stand in contact for 3 hours at 83° to 85°C. To 25 cc. of the filtrate was added 25 cc. of 10 per cent cane sugar solution, and then heated for 3 hours as usual. The amount of sugar inverted is recorded, together with the amount of sugar inverted by the same soil in mass in 1½ hours (taken from Experiment 1). These results are corrected for the amount of invert sugar present in the cane sugar itself, and in some cases by a small figure representing the reducing power of the water extracts of the soils.

SOIL	SUGAR INVERTED BY WATER EXTRACT FROM 5 GM. OF SOIL	SUGAR INVERTED BY SOIL ITSELF (SEE EXPERIMENT 1)
	gram	*gram*
P2	0.0009	0.1132
Turkey Hill, 0	0.0026	0.0986
P3	0	0.0680
724	0.0014	0.0510
P1	0.0055	0.0228
Muck, 1713	0	0.0277
Muck, 1711	0	0.0193

It is seen that water extracts from only a few of the most acid soils have any inverting power, and that insignificant when compared with the power of the soil itself. This is in agreement with conclusions usually drawn concerning the reaction of water extracts of soils. It is probably only where air and water movement in a particular soil are restricted, or under other peculiar conditions, that water-soluble acids can form and accumulate (31). But on the other hand, water extracts of the most acid soils, when boiled to remove carbon dioxide, have been usually found to be alkaline (22, 63, 97). As will be referred to again later, the use of the hydrogen electrode in determining hydrogen-ion concentrations of soil suspensions seems, at first sight, to yield contradictory results, but it must be remembered that these measurements have been made upon suspensions and extracts in the cold and containing carbon dioxide in considerable quantities. This is an acid, and cannot but have some influence upon the hydrogen electrode, yet cannot be said to be an undesirable constituent of soil systems. At the temperatures used in digestions with cane sugar, carbon dioxide would be driven off, and could not therefore be a factor in the inversion reaction.

Consideration of the second possibility led to the following experiment.

Experiment 3

Five-gram portions of two moderately acid New York soils were heated with 50 cc. of a 10 per cent cane sugar solution at 83° to 85°C. After *2* hours the soil was filtered away, and the amount of sugar that had been inverted determined in aliquots of the filtrates: Soil A, 0.0369 gm. per 50 cc.; Soil B, 0.0563 gm. The remainder of the filtrates were further heated for 1*2* hours and the invert sugar again determined: A, 0.0377; B, 0.0546. Other digestions were prepared with identical conditions except that the soils remained in contact with the solutions for the entire 2 hours; the amount of sugar inverted by Soil A was 0.0561 gm., and by B, 0.0848 gm.

These results show that no continued inversion took place in the sugar extract after the soil was removed, therefore there could not have been any acid extracted. Yet when the soil was in contact with the solution the whole

time much more invert sugar was produced, indicating again that the active agency remained with the soil mass.

ACTIVITY DUE TO THE SOLID PHASE

Experiment 4. A study of the amount of inversion produced by varying quantities of the same soil

All sugar solutions were prepared containing 10 per cent of cane sugar. To 50-cc. portions, different quantities of soil were added as indicated. The time of digestions was 1½ hours, and the temperature was kept at 83° to 85°C. Results are given in grams of sugar inverted in the 50 cc.:

AMOUNT OF SOIL ADDED	SOIL P1		SOIL P3		SOIL 724	
	Invert sugar	P (H)	Invert sugar	P(H)	Invert sugar	P (H)
grams	*gram*		*gram*		*gram*	
1	0.0107	7.07	0.0340	7.07	0.0342	6.98
2	0.0159	7.07	0.0680	7.07	0.0653	6.98
4	0.0188	7.09	0.0816	7.07	0.0673	6.98
8	0.0367	7.07	0.1088	7.07	0.1061	6.98
16	0.0612	7.07	0.1061	7.07	0.1115	6.98
32	0.1295		0.1134	7.07	0.1360	6.98

According to the hypothesis of Guldberg and Waage (65), "the active masses of solid bodies which participate in a chemical equilibrium are constant." It should be specified, however, that this applies where the activity of the solid is due only to that part which passes into solution. For, if there is present a saturated solution, its concentration must, of course, be independent of the amount of solid present over and above that necessary to produce it. If the soluble part only enters into the reaction, then, barring secondary effects, the action will be the same whether the amount of solid present be much or little. But, on the other hand, if the solid phase is active in the reaction, then, the extent to which such a reaction proceeds will depend upon the amount of that solid present. If soils are considered as containing very slightly soluble acids, then the quantity of acid in solution will not be different whether 1 or 32 gm. of soil stand in contact with a given amount of water, and therefore there should be the same amount of inversion by soils whether 1 or 32 gm. are used. The above results show that this is not the state of affairs but that the amount of inversion depends upon the amount of soil present The only interpretation that can be made, then, is that the solid phase itself is the active factor in inverting cane sugar, and not the solution phase of some highly insoluble acid.

While the quantity of sugar inverted depends upon the amount of soil present in contact with the solution, it is noted that the hydrogen-ion con-

centration of the extracts is independent of this ratio—remaining the same whether 1 or 32 gm. of soil stand in contact with 50 cc. of solution. Similarly, Sharp and Hoagland (83) found "comparatively insignificant changes in the H-ion concentrations when widely varying proportions of water to soil are used." These facts bring out very strikingly that that acidity which is bound up with the soil mass is independent of the character of the solution standing in apparent equilibrium, and that such acidity cannot be measured by determining the hydrogen-ion concentration of the solution in contact with that soil.

Experiment 5

If the active agency in the inversion of cane sugar is the soil particles themselves, then the reaction must take place at the surface of the particles only. In such a case the rate of inversion would depend upon the rapidity with which the inverted sugar diffused away from this region, and with which the sugar unacted upon diffused toward it (64). It was thought that shaking might hasten the inversion, therefore, by causing the soil surfaces to come in contact with fresh solution oftener than would happen if the mixture were allowed to stand quietly. As the digestions in this experiment took place at room temperature, but little total inversion was found; however, the amount of invert sugar produced is seen to be very much greater where the samples were shaken:

SOIL NUMBER	STANDING 24 HOURS	SHAKING 9 HOURS; STANDING 16 HOURS
	gram	*gram*
1	0.0085	0.0238
2	0.0085	0.0293
6	0.0031	0.0146
9	0.0097	0.0287

Experiment 6

Here an attempt is made to lessen the inverting power of soil by repeated extractions with water and with sugar solution. Five-gram portions of soils were heated on a water bath for 2 weeks with (a) water, and (b) 5 per cent sugar solution. Every day the supernatant liquid was poured off and replaced with fresh. Finally, the inverting powers of the residues were determined, and compared with that of the same soils untreated: Soil 2 untreated, 0.2744 gm. sugar inverted; same extracted with water, 0.1945 gm.; same extracted with sugar solution, 0.1400 gm. Soil 9 untreated, 0.1689 gm.; same extracted with water, 0.1066 gm.; same extracted with sugar solution, 0.0866. Soil 12 untreated, 0.1215 gm.; same extracted with water, 0.0955 gm.; same extracted with sugar solution, 0.0982 gm. Soil 15 untreated, 0.1360 gm.; same extracted with water, 0.0867 gm.; same extracted with sugar solution 0.0870 gm.

In this as well as in other experiments, where long continued extraction of soil has been employed, it has never been found that the inverting power can

be reduced to zero, though as is seen, in some cases a very insignificant reduction can be effected. During the long continued extraction treatments at high temperatures, it is probable that many changer are taking place at the surface of the soil particles, and that the loss in inverting power is due more to this than to a dissolving away of the soil acid.

In the above experiments, many cases are found where inversion by a soil took place, and at the same time the extract was alkaline, i.e., $P(H)$ less than 7.07. This may seem strange—that there should be solution of free base, yet the soil standing in contact with this solution and presumably in equilibrium with it, should behave as an acid. The following experiment shows this even more strikingly.

Experiment 7

Five-gram portions of acid soils were treated with 0, 5, 10, 15, 20 cc., respectively, of saturated lime water, evaporated to dryness, and the inverting power of the residues tested, by digesting under the usual conditions with 50 cc. of 5 per cent sugar solution. The amount of the sugar inverted and also the hydrogen-ion concentration of the extracts are recorded:

SOIL	LIME WATER ADDED	SUGAR INVERTED	P (H)
	cc.	*gram*	
Nara	0	0.3092	6.90
	5	0.0456	7.24
	10	0.0081	7.50
	15	0.0060	7.85
	20	0.0038	8.30
Kubiki	0	0.2928	6.98
	5	0.1557	7.05
	10	0.0890	7.25
	15	0.0840	7.25
	20	0.0340	7.35
Yamaguchi	0	0.3972	6.90
	5	0.1998	6.95
	10	0.0869	6.96
	15	0.0393	7.25
	20	0.0033	8.04
Matsuyama	0	0.0668	6.98
	5	0.0150	7.35
	10	0.0075	7.50
	15	0.0069	7.65
	25	0.0018	8.30

Here it is shown again that a soil may be in equilibrium with an alkaline solution and still exhibit marked acid properties, such as inverting action on sucrose.

Thus far it has been definitely established that inversion by soil is due almost entirely to something intimately bound up with the solid particles themselves, and in very small measure indeed, to anything passing into solution.

The next experiments were prepared with the idea of testing the action on sugar, of substances, the composition or condition of which is understood, that it might be reasoned by analogy to what the inverting power of soils is due.

INVERSION BY OTHER SOLID SUBSTANCES

Experiment 8

A large number of insoluble substances were tested for their activity on cane sugar. The strength of the sugar solution was 10 per cent, 50 cc. being used, and the temperature of digestion was 83° to 85°C.:

MATERIAL	AMOUNT USED	DURATION OF DIGESTION	SUGAR INVERTED
	grams	*hours*	*gram*
Alumnia (Kahlbaum)	5.0	3	0
Silicic Anhydride (Kahlbaum)	5.0	3	0
Filter paper	0.5	2	0
Cotton	3.0	2	0
Asbestos	2.0	3	0
Sulphur	5	2	0
Fuller's earth A	5	3	0
Fuller's earth B	5	3	0
Pumice stone	5	3	0
Charcoal	5	2	0
Bone black	5	2	0
Potter's clay	5	1½	0
Dicalcium phosphate	5	1	0.0622
Stearic Acid	5	2	0.0886
Casein	5	3	0.0425
Tannic acid	5	3	2.2356
Kaolin A	5	3	0.0358
Kaolin B	5	3	0.3060
Colloidal silicic acid*	25 cc.	3	0.0792
Humic acid†	1	3	0.4713
Barium sulfate (a)‡			0
Barium sulfate (b)‡			0.2055

* Prepared by acidifying a solution of water-glass with hydrochloric acid and carefully dialyzing until all chloride was removed.

† "Humic acid," also casein, were washed until apparently free from soluble acid.

‡ Barium sulfate (a) was precipitated in the presence of hydrochloric acid and washed until apparently free from chlorides. Barium sulfate (b), was precipitated in a neutral solution. Equal quantities of (a) and (b) were used.

Some rather unexpected results were here obtained. Fuller's earth, which has often been put forward as having characteristics similar to acid soils (63), likewise cotton (21) and charcoal (22), did not invert, neither did Kahlbaum's

silicic anhydride, though it will be shown later that in the latter case action may have been prevented by impurities. Dicalcium phosphate inverts, though the dibasic alkali phosphates do not. There was probably a decomposition of the dibasic calcium phosphate with the formation of some monocalcium phosphate which caused the inversion.[4]

If it is true that inversion is caused only by acid, then casein, tannic acid, colloidal silicic acid and humus must be themselves acids or must contain adsorbed acids. The behavior of barium sulfate would point to the latter possibility.

This led to the study of the action of materials containing adsorbed acids, and experimentation was made in many ways. It was often found that after solid materials had stood in contact with acid solutions, then washed until the washings no longer gave tests for the acid and showed hydrogen-ion concentration to be the same as that of pure water, they still had a strong inverting action on cane sugar. The following is an example of many such experiments performed, all of which will not be recorded here.

Experiment 9

Aluminum oxide was allowed to stand in contact with dilute hydrochloric acid solution; barium sulfate was precipitated in presence of an excess of hydrochloric acid, and lead sulfate in presence of sulfuric acid. All were washed with water and with cane sugar solution until the washings gave no tests for chlorides or sulfates. Action on sucrose was then tested for in the usual manner. Aluminum oxide inverted 0.0128 gm. of sugar, the extract giving a hydrogen-ion concentration of 7.24; barium sulfate, 0.0106–7.10; lead sulfate 0.0442–7.10.

Similar experiments with charcoal showed that the acid was more easily washed out, and by the time the washings became just neutral, it had no inverting action. Attempts to show that carbon dioxide adsorbed on charcoal, barium sulfate, lead sulfate and sulfur could invert sucrose gave negative results. These materials were suspended in water and carbon dioxide gas passed for a long time, but the materials thus treated would not invert. Such behavior was not anticipated, since under other conditions carbon dioxide has been found to have inverting power (2).

The above results show that solid materials can so bind soluble acids that they may not be removed with water, in any measurable degree, but still will invert cane sugar when allowed to come in contact with that solution.

ACTION OF THE ELECTRIC CURRENT IN DECOMPOSING SUBSTANCES IN SUSPENSION

If any slightly soluble salt such as tricalcium phosphate or barium sulfate is placed in the lower part of a U-tube, covered with water, and direct current

[4] In this connection see Joly and Sorel (43).

passed by immersing electrodes in the upper arms of the U-tube, it will be found that the salts are rapidly decomposed, the base moving to the cathode, and the acid in the opposite direction.

Such action of the current on silicates was observed by Brongniart and Malaguti in 1843 (20). Similar experiments on soils were performed by König, Hasenbäumer and Hassler (48), who believed that adsorbed elements, especially bases, were forced from their combination with the soil complex in this way. However, there seems never to have been made a study of the silicate residue after such treatment. In the following experiment a number of soils and allied substances were extracted with an electric current, and the behavior of the residues tested.

Experiment 10

The materials to be studied were placed in U-tubes, the arms sometimes being filled halfway. The tubes were filled with water and electrodes from a 110-volt direct current allowed to dip just under the water. From time to time the water was removed from both arms and replaced with fresh. Solutions from the cathode compartment were always found to be alkaline to phenolphthalein and that from the anode side sometimes, but not always, acid to neutral red. After the current had passed for a long time and the water had been replaced a number of times, it was found that less and less base was forced into the cathode side. Tests of the activity of the residues upon sugar were made, and compared wth the action of a similar amount of untreated material; P(H) of the sugar extracts are also recorded in the following table.

The results show that silicates can be rendered active on cane sugar by the action of the electric current, when the original substance had no such action.

In every case the solution in the cathode compartment became alkaline rapidly and strongly; acid could sometimes be detected in the anode side but was never so marked as the alkalinity of the cathode compartment. This splitting off of base together with the increase in acidity of the residue, would point to a breaking up of the silicate, silicic acid remaining behind in the residue, to which would be attributed its inverting power. On the other hand, there is the possibility that impurities might be present, such as chlorides, sulfates and phosphates, which were decomposed by the current—the bases passing into solution while the acid was adsorbed by the silicate complex. One would then attribute the inverting power of the residue to this adsorbed acid. As is seen from previous experiments, adsorbed acids do very readily invert cane sugar, and if such an adsorption of acid had taken place, this would be sure to follow. However, many investigators have shown that the silicate complex universally adsorbs base in preference to acid, so that there is the greatest reason for believing that if, for instance, tricalcium phosphate were present and decomposed by the action of the current—if the calcium were not adsorbed by the silicate, then neither would be the acid. This leaves the other alternative—that in the silicate residue insoluble silicic acid is left, after the

base with which it was in combination is driven out by the current, and it is this silicic acid which catalyzes the reaction of cane sugar inversion.

In an attempt to prepare silicic acid in such a manner as to preclude the possibility of any other acid being present, the following experiment was carried out. Starting with Kahlbaum's "silicic anhydride," which is seen to be impure, for a large amount of base may be extracted by the current, a quantity was boiled with concentrated nitric acid, filtered, and washed with water.

MATERIAL AND TREATMENT	SUGAR INVERTED PER 50 CC.	P(H)
	gram	
Soil 12, original	0.1698	7.09
Same, extracted 3 days	0.1954	7.09
Soil 10, original	0.1644	7.09
Same, extracted 3 days	0.3306	7.08
Soil 11, original	0.1884	7.09
Same, extracted 3 days	0.4094	7.09
Soil 13, original	0.1810	7.09
Same, extracted 3 days	0.2611	7.09
Orthoclase, original	0	7.27
Same, extracted 6 days	0.0320	7.14
Same, extracted 30 days	0.1040	7.09
Appophyllite, original	0	7.35
Same, extracted 6 days	0.0090	7.16
Same, extracted 30 days	0.0300	7.14
Albite, original	0	7.28
Same, extracted 6 days	0.0168	7.14
Same, extracted 30 days	0.0334	7.14
Olivine, original	0	7.24
Same, extracted 6 days	0.0050	7.16
Fluoridin, original	0	7.86
Same, extracted 3 days	0.0220	7.14
Water-glass very dilute, original	0	alkaline
Same, extracted until free from base	0.0300	7.07
Fuller's earth, original	0	7.76
Same, extracted 3 days	0.0140	7.14
Kahlbaum "silicic anhydride," original	0	7.14
Same, extracted 3 days	0.5375	7.07

A portion of this was tested by extracting with the current to find whether or not all base had been removed. The acid treatment was repeated as well as the testing until all base had been removed. The material was then dried and ignited until it showed no inverting action on cane sugar. (At this point there must have been pure silicic oxide free from base or any acid substance.) This was suspended in dilute sodium hydroxide in a beaker, the electrodes allowed to dip in the solution, and the current passed. By this treatment, it was hoped that some of the silicic oxide would be changed to sodium silicate. After several days of this treatment, the whole was transferred to a U-tube and the base removed by action of the current as already described. The

residue was then found to invert cane sugar very strongly, the extract showing a neutral reaction. That it is possible to have an insoluble silicic acid which inverts cane sugar is proven, and it must be concluded from the above considerations, that the presence of such in acid soils is a strong possibility.

Many attempts were made to prepare an "aluminic acid" in the same way, but without success. Such a substance, if it exists, does not invert cane sugar, and cannot be a factor in the inverting action of soils.

HYDROUS OXIDES ON CANE SUGAR

Lindet explained the inverting power of some metals as probably being due to the formation of hydrous oxides, which in some way liberated acid hydrogen. Copper, lead, tin, bismuth, aluminum and antimony were thus believed by him to cause inversion.

Hydrous oxides of lead, copper, bismuth, alumium, zinc and iron have been prepared, unusual precautions being observed to preclude the possibility of having impurities of adsorbed acid or base present. None has been found to have inverting power. Oxides of iron and aluminum in soils, therefore, cannot be factors in catalyzing this reaction.

INVERSION AND SELECTIVE ADSORPTION

There are many examples in colloid chemistry of solid materials selectively adsorbing or removing from solution either the base or the acid part of a neutral salt, leaving the other in solution. This is explained, by postulating that the salt reacts with water in a greater or lesser degree, depending upon the "strength" of its constituents, forming basic hydroxide and free acid. Of course, there is always the tendency for these to unite again and the reaction to go in the opposite direction. Allowing M R to represent a salt in solution, the reaction would be:

$$MR + HOH \rightleftarrows MOH + HR$$

Solid materials in contact with liquids are thought to bear electric charges at their surfaces. If the solid is negatively charged it will adsorb from salt solution the basic hydroxide, if positively charged, the acid will be removed. The supernatant liquid in the former case would be acid, and in the latter, alkaline. The removal of either base or acid would allow more salt to hydrolyze, and this action would continue until such high concentrations of acid or base had accumulated that further action would be prevented. Soils, and in fact, most solids, in contact with water bear negative charges. If they are allowed to stand in contact with neutral salts, the base is removed, and the acid accumulates in the supernatant liquid.

In systems where this absorbing effect is strong, the acid may be easily tested for by means of indicators, but where it is very slight and indicators fail, the inversion test should furnish a means for detecting the acid.

Experiment 11

To 50-cc. portions of a 10 per cent cane sugar solution, containing also 7 per cent of potassium chloride, were added various substances in amounts indicated, and digestions allowed to proceed at 83° to 85°C. for 3 hours. Similar digestions were prepared except that no potassium chloride was present. The amount of sugar inverted per 50 cc. is recorded:

SOLID PHASE	AMOUNT	SUGAR INVERTED; KCl NOT PRESENT	SUGAR INVERTED; KCl PRESENT
	grams	*gram*	*grams*
Cotton	2	0	0.0226
Sugar charcoal	5	0	0.0173
Filter paper	1	0	0.0302
Sulfur	5	0	0.0444
Asbestos	2	0	0.0943
Silicic anhydride	5	0	0.0948
Fuller's earth, no. 1	5	0	0.0475
Fuller's earth, no. 2	5	0	0
Kaolin, no. 1	5	0.0358	0.1574
Kaolin, no. 2	5	0.3060	0.9180
Casein	5	0.0425	0.2599
Humic acid	5	0.4713	0.8954
Colloidal silicic acid	25 cc.	0.0792	1.1782

These results show how it is possible to have inversion take place through the acid resulting after the selective adsorption by negatively-charged insoluble substances of the basic part of the neutral salt. In the following experiment a much lower concentration of salt is used, and the action of soils is recorded.

Experiment 12

Five grams of soil were added to 50-cc. portions of a 5 per cent cane sugar solution containing also 30 parts per million of potassium chloride. Digestions took place at 83° to 85°C. for 1½ hours. At the same time checks were run with no potassium chloride present. Results are given in grams of sugar inverted per 50 cc.:

SOIL NUMBER	SUGAR INVERTED; KCl NOT PRESENT	SUGAR INVERTED; KCl PRESENT
	gram	*gram*
1	0.2040	0.2414
8	0.1020	0.1326
9	0.0884	0.1210
10	0.1054	0.1414

In a similar manner, digestions were run in which 0.07 per cent of calcium sulfate was used instead of potassium chloride:

SOIL NUMBER	SUGAR INVERTED; $CaSO_4$ NOT PRESENT	SUGAR INVERTED; $CaSO_4$ PRESENT
	gram	*gram*
1	0.2040	0.2528
8	0.1020	0.1700
9	0.0884	0.1326
10	0.1054	0.1516

The effect of the addition of 0.1 per cent of tricalcium phosphate was tested similarly. Soil A with no addition inverted 0.0405 gm. of cane sugar, with tricalcium phosphate added, 0.0450 gm.; soil B, similarly, 0.0485 and 0.0589 gm.

Soils in contact with weak solutions of potassium chloride, calcium sulfate, or with tricalcium phosphate present, exhibit considerably greater inverting power than when alone, showing again a selective adsorption of base. Salts in such concentrations as these may always be found in soil solutions. It should be concluded, therefore, that inversion of cane sugar by soils may be due in part to the acid set free after the selective adsorption by the soil of base from any neutral salt that might be present.

It is entirely probable that a part of that acidity obtained by the hydrogen electrode in contact with soil suspensions results from such a reaction as this. In such cases, this effect might be produced by the action of some slightly soluble salts of the soil, or, which would surely be the case if considerable care were not taken in carrying out such determinations, the neutral salt (KCl) in tubes used in making contact to the calomel electrode would diffuse to the region of the soil, and an acid would then be formed, either through selective adsorption as just described, or through a modification of this phenomenon—basic exchange (77).

DISCUSSION

Significance of the inverting power of soils

In this paper it has been brought out that insoluble silicic acid and adsorbed acids, as well as soluble acids, may invert cane sugar. As it has never been proven that this reaction can be catalyzed by any other inert substance than acid, the inverting power of soils must be an indication of the actual acid there.

Probably there has never been another method used in the study of soils that measures the relative amounts of *true* acid. A possible exception is the method suggested by Conner (26), which determines the saponification of ethyl acetate in contact with soils, though he did not prove that there were not other substances in soils than acid which could cause or aid this action. The determination of hydrogen-ion concentration by the hydrogen electrode in contact with a suspension of soil in water has been used by Saidel (80), Fischer (30), Gillespie (34), Sharp and Hoagland (83), and Plummer (72).

It is claimed for such results that they represent the "intensity of acidity" rather than the "quantity of acid" present (35). At any rate, it is evident that this "intensity of acidity" as measured by the hydrogen electrode can be only that which is in the solution phase, and that this acidity is not necessarily dependent upon that acidity which is bound up with the soil solid phase. Experiments 1, 4, 7 and 10 have shown that they are not dependent. Indeed, a soil may be of such nature as to yield an alkaline solution to water, and still have acid properties. Similarly, the results obtained by Bovie (17) show that adsorbed acids are not detected by the hydrogen electrode. Therefore, acidity of soil extracts as determined by the hydrogen electrode cannot be a measure of that much larger acidity—that which does not pass into solution. On the other hand, the inverting power of soils is due chiefly to this acid—insoluble and adsorbed.

Quantitative considerations

Only in a general and comparative way may quantitative interpretations be placed on the results recorded in this paper. Quantities of cane sugar inverted by different soils under identical conditions are indicative of the relative amounts of the acids therein, but it would be impossible to draw conclusions as to the absolute amounts of acid present, since, as is seen from experiment 4, the amount of sugar inverted varies with the amount of soil in contact—and yet not in direct ratio. However, some idea may be obtained of the acid equivalent of these soils by comparing their inverting powers with that of acid of known strength under identical conditions. The following shows the amount of sugar inverted by hydrochloric acid of different strengths. Fifty cubic centimeter portions of 10 per cent sucrose solutions containing acid of strengths indicated were heated for 1½ hours at 85° to 87°C., and the amount of sugar inverted then determined: N/100 HCl, 1.815 gm. sucrose inverted; N/1000, 0.7141; N/5000, 0.2496; N/10,000, 0.1196; N/20,000, 0.0323; N/40,000, 0.0236; N/100,000, 0.0101. Comparing these figures with results obtained in experiment 1, it will be seen that 5 gm. of most of the acid soils effect greater inversion than is produced by N/20,000 acid which was found by Cameron and Breazeale (23) to be injurious to clover, and judging from the results of experiment 4 it is probable that all soils studied could be made to invert much more than this amount of cane sugar if larger quantities were used.

It is, of course, not fair to conclude that the acid present in the soil mass, and producing the inverting effect, is as injurious to plants as such a soluble and highly ionized acid as hydrochloric acid. Yet it must be recognized that while soil acid itself is not in solution, such large amounts of this acid are often present as to be potentially equivalent to a soluble acid of too high concentration to permit satisfactory plant growth. If not having a direct injury on the plant, this insoluble acid must injuriously modify the character of the soil solution.

Adsorptive power

While true insoluble acid may make for infertility, directly or indirectly, there are other properties that a soil may have that contribute to this condition, and may even be dominant. Many substances, including most soils when in contact with a solution containing a basic element, have the power of removing a part of that element from solution, and holding it more or less tenaciously against the leaching effects of water. Where the solid material contains acid, this action is due no doubt in part to it, but there are many examples recorded in the literature of colloid chemistry, where substances containing no acid exhibit this phenomenon as well.

This adsorptive force, distinct from the condition of acidity, has previously been recognized in soils. "Absorptiv ungesättigte" (74), and "negative acidity" (59) are terms aptly used to describe it. That there is not necessarily any relation between this force and acidity, is brought out especially in the behavior of muck soils. When these are tested for inverting power, relatively little is found, yet it is well known how strongly this type of soils removes free base from alkaline solution.

On account of the fact that base is found to be attracted and held through the adsorptive power of soils, and since such would be expected of an insoluble acid, it has sometimes erroneously been assumed that insoluble acid is the only cause. Some have calculated the amount of acid which would necessarily be present to unite with the same amount of base as they found soils to combine with (81, 92, 96). These figures run so high that it would be ridiculous to conclude that such amounts of acid are really there.

As to the nature of this adsorptive force, whether chemical or physical there has been much speculation (3, 8, 14, 18, 32, 94, 105 and others). However, recent views (6, 10, 38, 51) concerning valence and attraction between molecules would lead to the conclusion that there may be really no sharp dividing line between chemical union and adsorption, which is generally considered to be due to a physical attraction, all such combinations differing only in degree. With this conception, it should properly be considered that bases are held in soils in every possible degree from loose to strong combinations, the strongest corresponding with that which is found in chemical compounds, the weakest being merely adhesions to the surfaces of particles, easily broken.

Amphoteric character of soils

Very significant were the results obtained in experiments 1, 7, and 10, where soils showed inverting power, and at the same time the digestion extracts were found to be alkaline. Similarly, Hanley found some soils to have inverting power which contained calcium carbonate. There is no doubt, then, that a soil may contain an acid and at the same time enough base to neutralize this acid without this neutralization ever taking place. This phenomenon is related to the fact that acid soils have been found to neutralize acid solutions partially

when brought in contact (16, 61, 77).[5] Similarly it can be shown that the inverting power of a mixture of an acid solution in contact with an acid soil is much less than the sum of their inverting powers as obtained separately:

Digestions were prepared of N/500 hydrochloric acid and 5 per cent cane sugar, with 5 gm. of different soils, and heated for two hours at about 85°C. Amounts of sugar inverted were: Soil A, 0.9248; Soil B, 1.0562; Soil C, 0.7912 gm. The acid alone was found to be sufficient to invert 1.0084 gm. of sugar under the same conditions, while Soil A alone inverted 0.5542 gm. of sugar; Soil B, 0.3819; and Soil C, 0.3316. There was considerably less inversion by the mixtures than might have been expected from adding the inverting powers of the two. Loss for Soil A + acid was 0.6378 gm.; Soil B, 0.3341; Soil C, 0.5488.

These facts would further show that true acidity in soil and the adsorptive process are separate and distinct, adsorbed bases in acid soils being capable of neutralizing soluble acid, and unless this is recognized soil behavior must seem paradoxical. Thus we would have a material which at once neutralizes an acid, apparently neutralizes a base when in contact with a base, and also inverts cane sugar. In this respect soils might be said to be amphoteric. Hundeshagen (41) reached similar conclusions and applied this term in his work upon kaolin.

Complexity of properties of the soil mass

Owing to the complexity of the soil mass and the widely differing properties of its constituents, there may be found yet other contradictory results. One need only try out all the methods for "soil acidity" on a given set of soils to see clearly that a soil may be classified as of high acidity by one method and low by another. Basic exchange with neutral salts (27, 40), or with basic salts (44, 56); adsorption of base from a solution of base (5, 16, 97), or of dyes (48); decomposition of insoluble carbonates (93), or soluble carbonates (42, 60); liberation of iodine from a mixture of potassium iodide and potassium iodate (13, 36), or from a mixture of potassium iodide with potassium nitrate (55), or with potassium nitrite (27); saponification of ethyl acetate (26)—are phenomena which have been made use of in indicating the quantity of acidity in soils, yet it cannot be said that these are all influenced by acid alone and no other factor; many soil properties or constituents are influential here. No doubt some of these phenomena are related, and as has been pointed out by one of us (77) and Kappan (47) there may be tendencies for equilibrium to be established between the various agencies effecting them, but there is no other reason why the different methods used in determining soil acidity should be expected to give parallel results.

A given method for soil acidity cannot determine the fertility or infertility of a soil but can measure only that particular property upon which that method is based. While many recent publications have suggested this point of view (7, 31, 82), there are other cases where, if the investigator had realized this,

[5] Somewhat contradictory results were obtained by Spurway (90).

he might have more easily and perhaps more correctly explained his results. Thus, Parker (70) has recorded a number of experiments of adsorption by soils of base from solutions containing both sodium hydroxide and potassium chloride. He explained his results on the basis of a correlated action, while it is probable that base is adsorbed from each more or less independently of the other, being due to different constituents in the soil.[6] Veitch and others (63, 98) point out that the organic part of soils has properties different from the mineral part, but this cannot be the whole story—both the organic and inorganic portions of soils must be thought of as made up of a large number of distinct substances, each with its individual properties, though of course often modified by the presence of the other constituents. Along this line have been a series of researches, first by Sjollema (84) pointing to the distinctive character of different soil constituents in removing dyes from solution.

On the other hand, there is danger of inaccurate application of this idea. The distinctions between "immediate" and "continuous" lime requirement (60), also "active" and "latent" soil acidity (96), which were based upon the idea that soils were, indeed, complex and that some soil constituents reacted more quickly than others when in contact with solutions, could possibly be better explained as merely a case of some time being necessary for the complete reaction of a single constituent, or set of constituents of the soil, with the solution phase. It has been shown by a number of investigators (11, 22, 24, 71) that in ordinary reactions between solutions and solid phases in contact, while the largest part of the reaction takes place at once, much longer time is required for a complete equilibrium.

General relation of base to soil fertility

If the amount of base present in the soil is relatively small, and the adsorptive power of the soil for that base is very strong, which conditions usually go together, then the soil will be found to be infertile; those elements, especially the bases, which are necessary for plant growth are so tenaciously held by the soil mass that the plant is deprived of nourishment. Such a soil will absorb base from solutions of bases or salts, will decompose carbonates, redden litmus paper, and may still contain no acid, though it usually does contain some, as was shown in the foregoing experiments. Barring secondary effects, and in general, the addition of any mono- or di-valent base[7] will improve a soil of this nature. Most soils contain much more of every element than is necessary for growing several crops, but if the total base present is insufficient to satisfy this excessive adsorbing power, these elements are held out from the soil solution as already described. On the other hand, if any strong base is added

[6] In this connection, see also Osugi and Uetsuki (68).

[7] Mono- and di-valent bases are specified since, as will be mentioned again later, iron and aluminum act differently, even injuriously. See also Daikuhara (27).

there is a tendency for other bases to be liberated. This is the basis for the common practice of the use of soil amendments.[8]

The situation with respect to bases, however, is by no means as simple as the above discussion might imply. Aluminum and iron are bases truly enough, yet their presence in soil solution is undesirable,[9] magnesium in large amounts may be toxic (12); excess of an alkali metal may cause an unfavorable physical condition, as witnessed in soils where large amounts of nitrate of soda had been applied, and an accumulation of the corresponding carbonate resulted; it is possible that there may be particular quantitative ratios between bases that are harmful (54); there have been recorded a few instances where soils are saturated with one base and yet basically deficient with respect to another (61). Neither should it be concluded that all soil infertility is to be attributed to an unsuitable condition among the basic constituents: Toxic organic compounds are often present (87); soils may be of such poor physical character as to hinder plant growth and nourishment; as is seen in alkali soils, an excess of any soluble salt renders the soil unfit for plants; also, under peculiar conditions soluble acid in unusual and injurious amounts must be admitted (31). Yet, for all ordinary crops, the base, lime, in even excessive quantities causes no injury, and it is found that most of the above-mentioned causes of infertility are ameliorated by an application of lime.

The behavior of iron and aluminum in soils especially forms an interesting chapter. These elements may be soluble in water alone (1, 78), or become soluble through an exchange with bases from fertilizer salts (27 63, 79). While iron and aluminum are present in soil particles in larger proportions than any of the other bases, they seem not to become active unless the other bases reach a relatively low figure, and may be placed in such a condition that they cannot influence the soil solution in any way if other (stronger) bases are plentifully supplied (63, 77, 79, 82, 90). As suggested by Daikuhara, a soil is never really basically "adsorptiv ungesättig" if iron and aluminum be considered as bases. In the event that stronger bases are in low proportions, iron and aluminum may then be free to exert their influence which is injurious in many ways: (a) as already mentioned, their ions are toxic to plants, (b) if they are present in solution as salts of strong acids, these hydrolyze, producing acid, and (c) in the event that other bases are not plentiful, phosphates may revert to iron and aluminum phosphates, in which condition phosphoric acid is most insoluble, and possibility non-available to plants (91, 104) Hence, a liberal application of a base, such as lime, in addition to preventing the solubility of iron and aluminum, also furnishes a base with which the phosphoric acid may combine, and remain in a comparatively soluble condition.

[8] While this is true in general, some cases have been reported where it does not seem to hold. See Lyon and Bizzell (58) and Briggs and Breazeale (19).

[9] For a review of the literature on this subject see Miyake (62).

"Acidity" is the term always applied when an infertile soil is made more fertile by the application of lime, but we must recognize that *acid* is only one of the factors causing this condition, and possibly even a minor one.

A method for the determination of relative soil acidity

Probably the only method ever developed for the determination of the true acidity of a soil depends upon the measurement of its catalytic activity upon the reaction of inversion of cane sugar. Acidity as here characterized is that which is due to soluble and insoluble acids. This is not acidity as it is ordinarily understood in soil literature and it is only one of the factors contributing toward that undesirable condition of soils found to be improved by the use of lime. Comparative measurements of true acidity of soils may be of value in some cases, when the following procedure is recommended: 5 to 10 gm. of soil is added to 50 cc. of a 5 per cent solution of cane sugar, the whole digested on a water bath at 80° to 87°C., from 1½ to 3 hours. The amount of sugar inverted is determined in the filtrate by the very delicate titrating method suggested by Cole (25).

SUMMARY

It has been shown that soils of many kinds and other insoluble materials can be made to invert sucrose; with soils this power is a property of the mineral portion as well as of the organic matter.

That this effect is due to acid cannot be doubted. This acid may be found in four different forms: (a) A slight quantity in a few soils is soluble in the sugar solution. However, the principal portion is bound to the soil particles; this may be in the nature of (b) acids which would otherwise be easily soluble, but are here strongly adsorbed on the soil particle surfaces, or (c) it may be of the nature of an insoluble acid such as silicic acid. Also, (d) a neutral salt present in the soil solution in even small quantities may be broken down while in contact with the soil mass, the basic part being more strongly adsorbed than the acid, when the latter is left free to exert its characteristic influence in inverting cane sugar.

That the inverting activity of soils is chiefly a property of the insoluble part was indicated in several ways. (a) Many soils showed inverting action on sugar in a solution which remained neutral after contact with the soil, or, in some instances, became alkaline. Also, similarly, when soil was allowed to adsorb some base, then digested with cane sugar solution, it showed inverting action, and also yielded up sufficient base to make the extract distinctly alkaline. (b) No inverting power, or very little, indeed, was found in water extracts from soils. (c) Inversion did not continue in sugar extracts after soils were removed. (d) Inversion increases with increasing amounts of soil in contact with the sugar solution, while there is no measurable change in hydrogen-ion concentration in the extract. (e) Greater inversion is produced by shaking soils with sugar solutions, than by allowing the mixtures to stand

quietly. (f) Long continued and repeated extractions of soils with water and with cane sugar solution did not greatly reduce their inverting power.

Fuller's earth, cotton, charcoal and other substances which have been described as similar to acid soils were found not to invert cane sugar.

Otherwise soluble acids so strongly adsorbed by solids as not to be removed by washing in any measurable quantity, will yet invert sugar in such condition.

Silicate minerals may be given inverting power by treating suspensions with direct current. Base is split off, passing into solution and to the cathode, and silicic acid remains with the mass, insoluble. Soil acidity is increased by a similar treatment of soils.

Contrary to previous conclusions, hydrous oxides of lead, copper, bismuth, aluminum, iron and zinc were not found to have any inverting power.

Many suspended substances having no inverting power alone, were found to produce inversion when a neutral salt was present, through selective adsorption of the base, thus setting a small amount of acid free.

"Soil acidity" is the term customarily applied when infertility of soil can be corrected by the use of a free base such as lime. There are many factors involved in causing this condition in soils, the presence of real acid being only one of them. Methods used for detecting or determining "soil acidity" generally do not measure the acid there but may depend upon many properties of soil mass in no way related to acidity. The power of a soil to catalyze the reaction of cane sugar inversion is a measure of its acid, and is probably the only method which can measure the acid bound up with the soil solid phase.

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THE PRODUCTION OF CARBON DIOXIDE BY MOLDS INOCULATED INTO STERILE SOIL

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Received for publication April 15, 1918

The purpose of the experiments reported here was to determine the physiological activity of certain molds when inoculated into sterile soil. It was hoped that such an investigation would throw some light on the question as to whether molds are active in soils and if they are, as to some of the products, chiefly carbon dioxide, of their life processes. Because of the excellent bibliography of the subject published recently by Waksman (2) we shall not go into the historical phase of the subject in detail here. In a review of the evidence and in consideration of results carried out in his laboratories, as to whether molds are present in soils in active form or not, Brown (1) shows that there is little to lead one to believe that molds are not active in soils. In this same paper, a brief review of the physiological activities of molds in soil, and their important bearing upon soil fertility, is also given.

Practically all of the work which has been done on the physiological activities of molds in soils has been carried out by using a sterile medium, usually soil, to which has been added some material, such as dried blood, in the case of a measurement of ammonification, and then inoculating with pure cultures of a mold or molds, the product sought being determined at the end of a certain period. There are two well recognized points of weakness in this procedure. First, sterilizing radically changes the soil, rendering plant-food and other material more soluble. Second, the addition of the large amounts of material (dried blood) makes the medium still further unlike typical soil conditions. The method which we used eliminated the second objection only. No method has yet been developed to render the soil sterile, and not radically alter its composition. In the last series of experiments reported in this paper, some progress was made in the solution of this problem.

EXPERIMENTAL

All the experiments were conducted with the apparatus shown in figure 1. Plate 1 gives the reproduction of a photograph of the whole arrangement of apparatus.

Experiment I

In this and the succeeding experiments, a clay loam soil with a lime requirement, by the Veitch method, of 1540 pounds of calcium carbonate per acre of

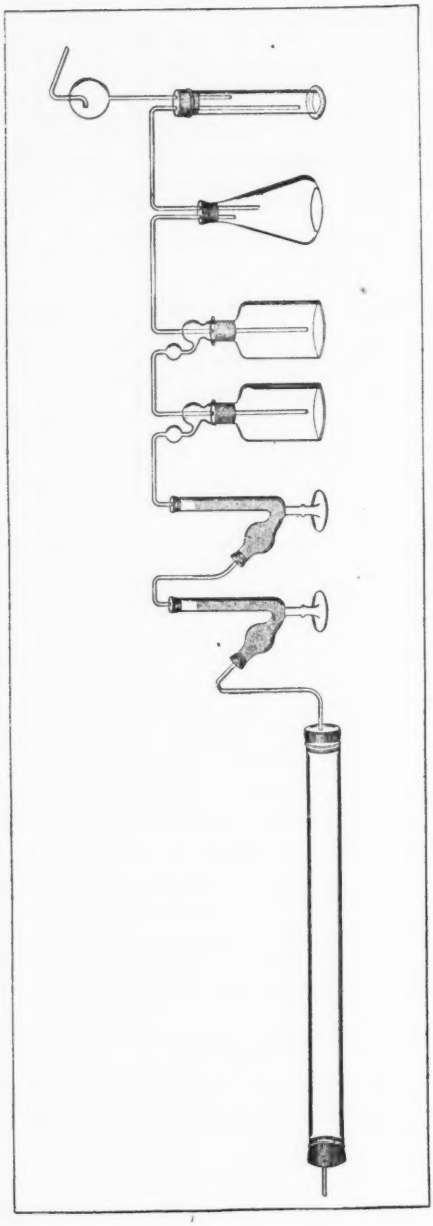

FIG. 1. DIAGRAM OF APPARATUS USED

2,000,000 pounds was used. After obtaining the soil from the field, it was partially air-dried, put through a ¼-inch sieve, and then completely air-dried and thoroughly mixed.

For Experiment I, 340-gm. (¾-pound) portions were weighed into 24 Erlenmeyer flasks, fitted with rubber stoppers and connecting tubes as shown in figure 1. The rubber stoppers were lifted about ½ inch out of the flasks and a large wad of cotton wrapped around the stoppers and tops of the flasks. The cotton was held in place by tying with string. The 24 flasks were then sterilized in the autoclave by steam at 10 pounds pressure for 3½ hours, three separate times, with 48-hour periods intervening between the autoclave treatments. After sterilization was complete the 24 flasks were placed in position, the cotton wads carefully removed and the rubber stopper placed in position. The cotton plugs in the ends of the glass tubes protected the flask and contents from contamination. The flasks were then inoculated as follows. The molds were isolated from this soil by means of successive plating on beerwort agar. After pure cultures were obtained, each culture was inoculated upon a thin layer of beerwort agar in a 500-cc. Erlenmeyer flask. After the cultures thus obtained had fruited well 300 cc. of sterile water was added and then a 75-cc. portion from the suspension of each mold was transferred under sterile conditions to each of two flasks of the sterile soil. Fifteen cubic centimeters of sterile dextrose solution was added to the remaining 150 cc. of water in the flasks containing the pure mold cultures. The dextrose solution was of such a strength that the solution in the culture flasks was made exactly 1 per cent dextrose. Seventy-five cubic centimeter portions were then transferred under sterile conditions to two more flasks of sterile soil. Before lifting the rubber stoppers from the flasks to add the inoculating liquid the stopper and the top of the flasks were swabbed with an alcohol-water (1–1) solution of mercuric chloride. The proper connections were then made in the apparatus and the air current was turned on. The inoculations were made January 25, 1916, and the air was run continuously over the soil until March 9, 1916. The carbon dioxide evolved was determined by titrations at intervals shown in table 1.

After the completion of the experiment, soils from the flasks were plated out on beerwort agar to test the purity of the cultures. This was done as follows. The flask was disconnected from the apparatus with the rubber stopper and entrance and exit tubes with the cotton plugs still securely fixed. The flask was then shaken violently. This left several grams of the soil adhering to the glass tube projecting below the rubber stopper. The tube with the soil was dipped into sterile water contained in a flask, whereupon most of the soil fell from the tube. Inoculations upon the plates of beerwort agar were made in the usual way. The results are found in table 1.

In table 1 will be found the amounts of carbon given off from the various soils as carbon dioxide. The total carbon also has been computed and ap-

TABLE 1

Amount of carbon evolved as carbon dioxide from soils in Experiment. (Results expressed in pounds of carbon per acre)

NO.	TREATMENT	REMARKS	DAYS AFTER INOCULATION																												TOTAL	AVERAGE
			1	Average	2–3	Average	4	Average	5–6	Average	7	Average	8–9	Average	10–11	Average	12–13	Average	14–17	Average	18–21	Average	22–25	Average	26–32	Average	33–39	Average	40–44	Average		
1	Mucor	Pure at end	307		133		76		73		22		55		47		25		55		42		63		151		100		44		916	
2	Mucor	Pure at end	40	35	88	110	50	63	79	76	26	24	54	54	47	47	21	23	55	55	43	42	57	60	134	142	125	112	65	54	883	899
3	Mucor, Dextrose	Pure at end	276		1,770		1,480		792		224		315		329		90		247		132		117		161		108		65		6,106	
4	Mucor, Dextrose	Pure at end	139	207	960	1,365	883	1,181	1,535	1,163	371	297	378	346	376	352	136	113	374	310	194	163	145	131	167	164	103	105	65	65	5,826	5,966
5	Rhizopus	Pure at end	143		269		107		58		22		63		75		41		156		69		54		108		74		36		1,275	
6	Rhizopus	Pure at end	89	116	94	181	82	94	87	72	23	22	66	64	96	85	43	42	148	152	74	71	75	64	122	115	91	82	51	43	1,141	1,208
7	Rhizopus, Dextrose	Pure at end	163		1,300		468		100		202		477		477		118		510		321		320		127		209		78		5,770	
8	Rhizopus, Dextrose	Pure at end	159	162	631	965	472	470	630	665	128	165	306	391	256	366	115	116	199	354	238	279	171	245	225	326	205	207	62	70	3,797	4,783
9	Aspergillus niger	Contaminated	77		248		178		164		76		138		158		50		197		90		137		258		73		34		1,878	
10	Aspergillus niger	Contaminated	65	71	322	285	298	238	236	200	110	93	282	210	293	225	96	73	199	198	87	88	120	128	200	226	90	81	51	42	2,449	2,163
11	Aspergillus niger, Dextrose	Pure at end	86		626		700		675		214		658		636		136		500		129		85		102		78		46		4,671	
12	Aspergillus niger, Dextrose	Pure at end	73	79	530	578	950	825	849	762	326	270	706	682	683	659	156	146	785	642	186	157	175	132	lost	102	185	81	56	51	5,664	5,167
13	Trichoderma	Pure at end (?)	42		228		129		127		30		82		49		24		168		80		53		100		87		52		1,480	
14	Trichoderma	Pure at end	40	41	55	136	64	146	196	161	52	41	55	68	73	61	37	30	150	159	63	71	72	62	147	123	103	95	71	61	1,177	2,378
15	Trichoderma, Dextrose	Pure at end	60		578		567		1,400		306		418		343		93		475		239		163		184		115		57		4,368	
16	Trichoderma, Dextrose	Pure at end	105	82	673	625	518	542	442	921	163	234	351	384	327	335	109	101	503	489	207	223	171	167	222	103	139	127	66	61	3,996	4,182
17	Chætomium	Pure at end	19		123		65		65		28		62		75		37		184		141		107		172		151		71		1,300	
18	Chætomium	Pure at end	18	18	131	127	67	66	213	139	143	85	216	139	78	76	39	38	192	188	197	169	159	133	141	156	149	150	65	63	1,808	1,554
19	Chætomium, Dextrose	Contaminated	28		404		240		155				690		648		128		589		221		292		413		386		186		3,836	
20	Chætomium, Dextrose	Pure at end (?)	32	30	354	379	344	292	395	275	213	213	326	508	502	575	187	157	730	659	310	265	168	230	378	395	404	395	213	199	3,899	3,867
21	Soil emulsion		135		323		190		205		69		101		121		77		225		154		139		236		170		92		2,236	
22	Soil emulsion		114	124	185	254	129	159	189	197	59	64	100	100	109	115	46	61	191	208	141	147	132	135	202	219	163	166	86	89	1,849	2,042
23	Soil emulsion, Dextrose		206		960		720		1,360		378		465		316		102		492		284		287		446		297		193		6,506	
24	Soil emulsion, Dextrose		186	196	660	810	627	673	1,280	1,320	337	357	567	516	306	311	128	115	474	483	286	285	288	287	415	430	299	298	190	192	6,043	6,274

pears in the last two columns of the table. The results obtained by plating out the soils also are given in the table.

It is seen that all the culture experiments involving the Mucor *Rhizopus* were found to be pure at the completion of the experiment. The two *Aspergillus* inoculated soils numbered 9 and 10, upon plating out were found to develop nothing but *Trichoderma* colonies. Since soils 11 and 12 remained pure with respect to the colonies of *Aspergillus*, it is quite certain that the inoculating culture was pure *Aspergillus*. There is nothing to indicate at what stage of the experiment contamination took place. Sterilization might not have been complete, although that is not probable. Contamination might have taken place during the inoculation or during the passing of the air over the soils or finally during plating.

All the *Trichoderma* inoculated soils remained uncontaminated, with the possible exception of no. 13. Upon plating this soil, one plate was found to develop nothing but *Trichoderma* colonies, another plate *Trichoderma* with a single colony of a *Rhizopus*, and the third plate mainly *Trichoderma* with a single colony of *Aspergillus*. Soils 17 and 18 were found uncontaminated, soil 19 showed mainly *Rhizopus* on the plates. No. 20 upon plating, gave one plate of pure *Chætomiun* colonies, another mainly *Chætomium* and a single *Rhizopus* colony, and the third mainly *Chætomium* with a single *Aspergillus* colony. Here, as with soil 13, it seems probable that the contamination was brought about during the plating.

The results obtained on the evolution of carbon, as carbon dioxide, will be discussed now. To facilitate comparison, the average amounts of carbon given per day for each period have been computed, and the results so obtained have been plotted, and appear in figure 2. Only the results for the soils with no dextrose have been plotted.

Perhaps the most noteworthy thing to be observed is the very rapid increase in the amount of carbon dioxide given off during the second and third day, and the fourth day. In every case, except the *Chætomium* cultures, there was a decrease on the fifth and sixth days. From the manner of inoculation, very great numbers of spores were added to the soils, and the rapid increase in amount of carbon dioxide evolved is no doubt due to the development of these spores. It has been found (3) that spore formation of fungi is accompanied or closely followed by a development of large amounts of ammonia. Probably there is also a development of a correspondingly large amount of carbon dioxide and our data might be taken to prove that, but there are other factors which enter in, which may have more influence. Sterilization of soil renders organic matter, and other nutrient material, more soluble, and therefore on the addition of large numbers of fungi spores, they immediately find a suitable medium for growth, hence they all develop vigorously. Later this nutrient medium becomes partially exhausted. It is seen from figure 2 that on the eleventh day two of the fungi, *Aspergillus* and *Rhizopus*, give an increased amount of carbon

over the previous period, while all of them give increased amounts during the period from the fourteenth to the seventeenth. This experiment which was carried out previous to the publication in regard to sporulation and ammonia

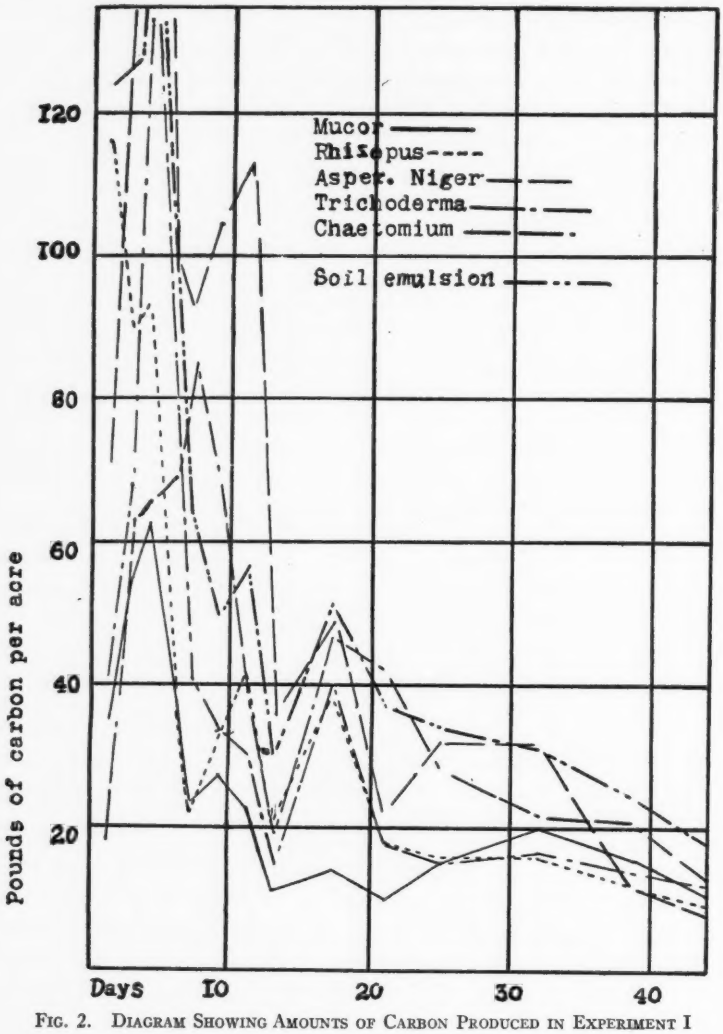

FIG. 2. DIAGRAM SHOWING AMOUNTS OF CARBON PRODUCED IN EXPERIMENT I

production (4), was subjected to the changing temperature of the laboratory, and hence many of the fluctuations observed were no doubt due to this factor. In general, the most valuable conclusion to be drawn from a consideration of

these results, as they appear in the table and in the curve, is that in some cases the fungi gave off more carbon than the soils inoculated with soil emulsion. In other cases, less is given, but in general the order of magnitude of the amounts is the same. More in regard to the significance of this will be said later.

The results for the soils to which dextrose was added, are in general similar to the results for the soil alone, except for the larger amounts of carbon given off. When the experiment was planned, it was not known whether or not the soil alone would support sufficient mold growth to give appreciable amounts of carbon dioxide, and this was the reason for using the dextrose.

At the end of the experiment, the soils were immediately air-dried, and later were analyzed for nitrate, ammonia, and soluble non-protein nitrogen.

Since the publication of the investigation which resulted in the proposal of the method for soluble non-protein nitrogen of soil (2), we have found that practically all of the nitrogen which is extracted by the 1 per cent acid belongs to this class of compounds. For example, in an examination of several soils, from 96 to 100 per cent of the nitrogen in the acid extract was not precipitated by 2.5 per cent trichloracetic acid. Therefore, the nitrogen extracted by the 1 per cent acid is always included in the soluble non-protein nitrogen group of compounds.

It should be stated that all results published by us on the soluble non-protein nitrogen except those in the original communication, have included in them the nitrogen of the acid extract. The value of the results in the original paper are in no way impaired by their incompleteness in this respect. A paper amplifying our first communication on soluble non-protein nitrogen is in course of preparation.

The results of these determinations are given in table 2.

The sterilized soil contained 0.895 per cent of the total nitrogen as nitrate nitrogen. The mold-inoculated soils in every case contained less nitrate nitrogen, and the dextrose-treated soils usually less than the corresponding untreated soil. These facts are in harmony with the findings of others, namely, that molds may reduce or utilize nitrates, and that so far no molds have been found which bring about nitrification. It is seen that there was a considerable accumulation of nitrates in the soil-emulsion-inoculated soils, except of course in the dextrose-treated flasks.

In the sterilized soil, 3.01 per cent of the soil nitrogen was present as ammonia. In the soils treated with the *Rhizopus* and the *Chætomium*, this amount was increased, while with the other molds, and the soil emulsion the ammonia was decreased. This decrease should not be interpreted as meaning that fungi might actually use more ammonia in the field than they would cause to be formed. The conditions would be quite different if nitrifying organisms were present to utilize the ammonia as it was produced. Higher plants would in some cases also function similarly. The reason for the great reduction in the amount of ammonia in the dextrose soils, is no doubt due to the greatly en-

hanced growth of the molds, which causes them to utilize a larger proportion of more easily available nitrogen present. Another factor should be taken into consideration in regard to the dextrose-treated soils. Undoubtedly there was a great initial increase in acidity from its decomposition and this would tend to make the growth and metabolism of the molds quite different from what would otherwise be the case.

TABLE 2

Nitrate, ammonia, and soluble non-protein nitrogen in the sterilized and unsterilized soil and in the sterilized inoculated soil after the completion of the experiment

NUMBER	TREATMENT	PER CENT OF TOTAL NITROGEN		
		Nitrate	Ammonia	Soluble non-protein
Original soil.....		0.325	0.60	14.45
Original soil.....	Sterilized.....	0.895	3.01	22.8
1, 2	Mucor.....	0.67	2.77	23.8
3, 4	Dextrose, Mucor.....	0.68	1.57	22.2
5, 6	Rhizopus.....	0.59	3.08	22.9
7, 8	Dextrose, Rhizopus.....	0.29	0.70	18.0
9, 10	Aspergillus.....	0.44	1.54	21.6
11, 12	Dextrose, Aspergillus.....	0.39	1.30	20.4
13, 14	Trichoderma.....	0.54	2.58	21.0
15, 16	Dextrose, Trichoderma.....	0.32	0.45	19.2
17, 18	Chætomium.....	0.65	3.64	21.9
19, 20	Dextrose, Chætomium.....	0.41	1.26	19.6
21, 22	Soil emulsion.....	2.98	2.56	18.9
23, 24	Dextrose soil emulsion.....	0.74	2.25	19.3

The sterilized soil contained 22.8 per cent of its nitrogen as soluble non-protein nitrogen. There was a slight increase in the amount caused by the *Mucor* and *Rhizopus*, while all the other fungi caused decreases. The greater the amount of the soluble non-protein nitrogen present, the less, of course, the amount of complex protein compounds, and therefore of soluble non-protein nitrogen present in this experiment will give an indication as to the amount of protein material synthesized or broken down. It is probably significant that those molds which give off the greater amount of carbon have apparently caused the synthesis of greater amounts of protein material. It is also seen that the soils treated with dextrose have in every case synthesized more protein material than their corresponding untreated soil. The reverse is true in the soil-emulsion-inoculated soils. In these soils bacterial action plays, no doubt, a large part. The synthesis of more protein complexes in the soil-emulsion-inoculated soils is to be explained by the fact that there are a multiplicity of varieties of organisms active in these soils.

Experiment II

In this experiment exactly the same arrangement of apparatus was used as in the previous experiment. The same fungi were used. Instead of employ-

ing dextrose, however, lime was used. This soil, as stated above, had a lime requirement by the Veitch method of 1540 pounds of calcium carbonate per acre. In order to make sure that sufficient lime should be added to the soils to render them basic, $\frac{3}{4}$ pound of the dry soil was mixed, with sufficient lime to give in one case an excess of $\frac{1}{2}$ ton and in the other of 1.6 tons, per acre. The soils were then heated in the autoclave 3 hours per day on three alternate days, and they were then tested with litmus paper. Since there was some question as to whether the soils receiving $\frac{1}{2}$ ton of lime in excess were alkaline, it was decided to use 1.6 tons of excess lime.

Twenty-four flasks were prepared as in Experiment I. To 12 flasks, lime in the amount indicated above was added, and the 24 flasks were sterilized simultaneously by heating 3 hours in the autoclave at 10 pounds pressure on three alternate days. After sterilization of the soils, the flasks were connected with the remainder of the apparatus, and 50 cc. of sterile water was added to each flask. Inoculation was not made until 15 days after this, air being forced over the soil, and into the alkali towers. This procedure was followed in order to make sure that sterilization was complete. The amount of carbon evolved in this preliminary period is given in table 3. On the fifteenth day, inoculation was made as before, except that only 20 cc. of the inoculum was used. This gave a final moisture content of the soil about the same as that of the previous experiment. Through an oversight, the soils were not plated out at the completion of the experiment; therefore, we cannot be certain that the cultures remained pure through the course of the experiment. It is thought that pure cultures remained in all the soils, for the following reasons. Table 3 shows that from the eleventh to the fourteenth day, of the 14-day period previous to inoculating the soils, no carbon was evolved from the unlimed soils. The amounts given during the first twelve days must have come from carbon dioxide held in the soil atmosphere and soil solution. The carbon dioxide, no doubt, came from the action of the heat on the soil organic matter. If any organisms had been present they soon would have multiplied enormously with a consequent rise in carbon-dioxide production. It is seen that some carbon dioxide was still being evolved from the limed soils during the last four days of the preliminary period, but only a small amount when compared with that given during the first 12-day period. Therefore, in the case of the limed soils, it seems safe to conclude that sterilization was complete. Successive platings of the inoculating cultures of molds invariably showed them to be pure. In all cases in this experiment, and the previous one on those soils inoculated with molds, the growth appeared on the surface of the soil a few days after inoculation. In the previous experiment on the soils where the molds remained pure throughout the experiment, no evidence of a foreign growth was ever seen, while in the few cases where the plating showed the presence of invading organisms, this was evident by a superficial examination of the soil during the course of the experiment. In this second experiment, the soil always showed evidence of the mold with which it had been inoculated, and in

TABLE 3

Amount of carbon evolved as carbon dioxide from soils in Experiment II. (*Results expressed as pounds per acre*)

NO.	TREATMENT	DAYS AFTER PLATING			DAYS AFTER INOCULATION																																TOTAL	AVERAGE
		1–9	11–12	13–14	1	Average	2–3	Average	4	Average	5	Average	6–7	Average	8–9	Average	10–12	Average	13–14	Average	15–18	Average	19–25	Average	26–32	Average	33–39	Average	40–47	Average	48–54	Average	55–61	Average		
1	Mucor	37	0	0	4		238		134		79		93		83		122		62		49		86		63		52		64		35		39		1,203	
2	Mucor	37	0	0	12	8	210	224	76	105	68	73	79	86	77	80	124	123	78	70	65	57	122	104	92	77	74	63	80	72	44	39	52	45	1,253	1,228
3	Mucor, Lime	170	0	0	33		175		67		65		87		139		220		90		85		58		76		71		76		42		60		1,344	
4	Mucor, Lime	284	1	0	10	21	147	161	75	71	67	66	87	87	150	134	143	183	54	72	42	63	899	73	76	76	59	65	63	69	35	38	58	59	1,155	1,247
5	Rhizopus nigricans	53	2	0	22		207		76		49		57		52		64		35		35		98		40	25	25		34		32		24		848	
6	Rhizopus nigricans	36	0	0	14	18	254	230	73	74	45	47	72	64	61	56	67	65	36	35	26	30	51	74	37	38	25	25	34	34	20	26	23	23	838	843
7	Rhizopus nigricans, Lime	362	14	10	12		189		72		57		71		195		122		44		35		208		92		28		95		50		49		1,319	
8	Rhizopus nigricans, Lime	169	7	0	15	13	204	196	67	69	52	54	72	71	65	130	80	101	35	49	26	30	50	129	40	66	27	27	41	68	28	39	30	39	832	1,075
9	Aspergillus niger	50	1	0	31		446		167		134		197		125		91		35		27		77		38		35		49		40		39		1,531	
10	Aspergillus niger	27	0	0	16	23	478	462	179	173	171	152	192	194	113	119	78	84	34	34	20	23	34	56	30	34	25	30	35	42	19	28	55	47	1,479	1,505
11	Aspergillus niger, Lime	371	28	10	92		625		106		77		77		74		81		42		41		121		51		43		44				32		1,538	
12	Aspergillus niger, Lime	415	28	10	33	62	491	558	121	113	103	90	95	86	73	73	76	78	33	37	25	33	64	92	38	44	34	38	44	44	32	28	47	39	1,301	1,419
13	Trichoderma	23	0	0	11		529		278		229		279		141		99		49		43		103		47		41		54		24		42		1,976	
14	Trichoderma	27	0	0	8	9	464	491	304	291	262	245	243	261	107	124	103	101	58	53	56	49	102	102	55	51	44	42	51	52	17	24	40	41	1,914	1,945
15	Trichoderma, Lime	458	27	14	105		504		149		138		197		149		130		61		52		120		60		51		61		46		49		1,872	
16	Trichoderma, Lime	347	0	0	10	57	330	417	271	210	244	191	215	206	106	127	97	113	66	63	57	54	118	119	65	62	55	53	64	62	34	40	46	47	1,878	1,925
17	Chætomium	26	0	0	2		79		67		65		89		100		102		72		66		125		75		54		58		34		33		1,018	
18	Chætomium	27	0	0	2	2	31	55	52	59	65	65	107	98	91	95	110	106	65	68	58	62	176	150	83	79	61	57	60	59	31	32	35	34	1,030	1,024
19	Chætomium, Lime	339	0	0	6		90		54		52		77		74		86		56		46		84		59		44		47		34		28		827	
20	Chætomium, Lime	313	2	0	17	11	100	95	58	56	57	54	101	89	87	80	181	133	76	66	5	49	132	108	75	67	61	52	79	63	24	38	74	51	1,202	1,014
21	Soil emulsion	26	0	0	4		26		167		160		334		248		225		83		108		235		136		121		150		52	87	139		2,225	
22	Soil emulsion	24	0	0	2	3	140	83	160	163	202	181	315	324	205	226	180	202	88		82	95	186	210	136	136	122	121	155	152	86	87	142	140	2,201	2,213
23	Soil emulsion, Lime	395	62	31	50		341		121		136		190		134		168		115	85	99		19		141		136		165		94		134		2,221	
24	Soil emulsion, Lime	383	43	17	17	33	285	313	191	156	158	147	160	175	155	144	165	166	112	113	112	105	238	217	159	150	139	137	168	166	97	95	126	130	2,282	2,251

no case was a foreign mold growth apparent. Of course, this is not absolute proof in regard to molds and no proof at all in a consideration of bacteria. However, it would seem probable that if foreign molds were kept out, bacteria would be also.

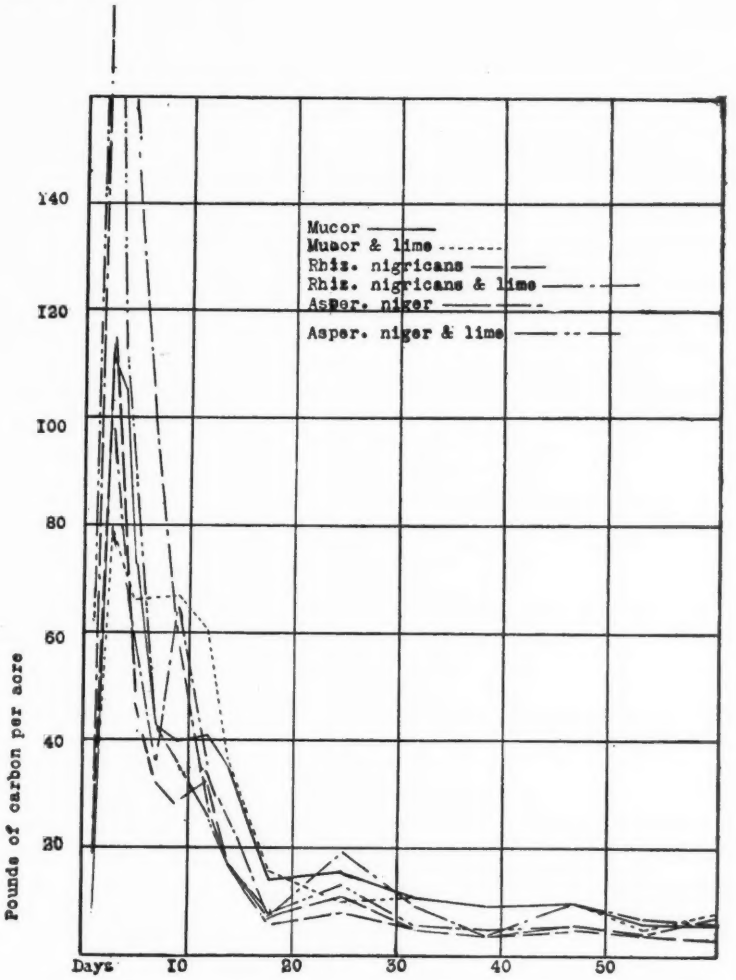

FIG. 3. DIAGRAM SHOWING AMOUNTS OF CARBON PRODUCED IN EXPERIMENT II

The amounts of carbon dioxide given from the various soils are set forth in table 3. The average amount evolved per day for each period has been computed, and the results so obtained were used in plotting the graphs in figures 3 and 4.

From the figures given in the last two columns of table 3 it is seen that the duplicates did not check very well in some cases, particularly for soils 7 and 8, and 19 and 20. No explanation of these discrepancies is apparent although

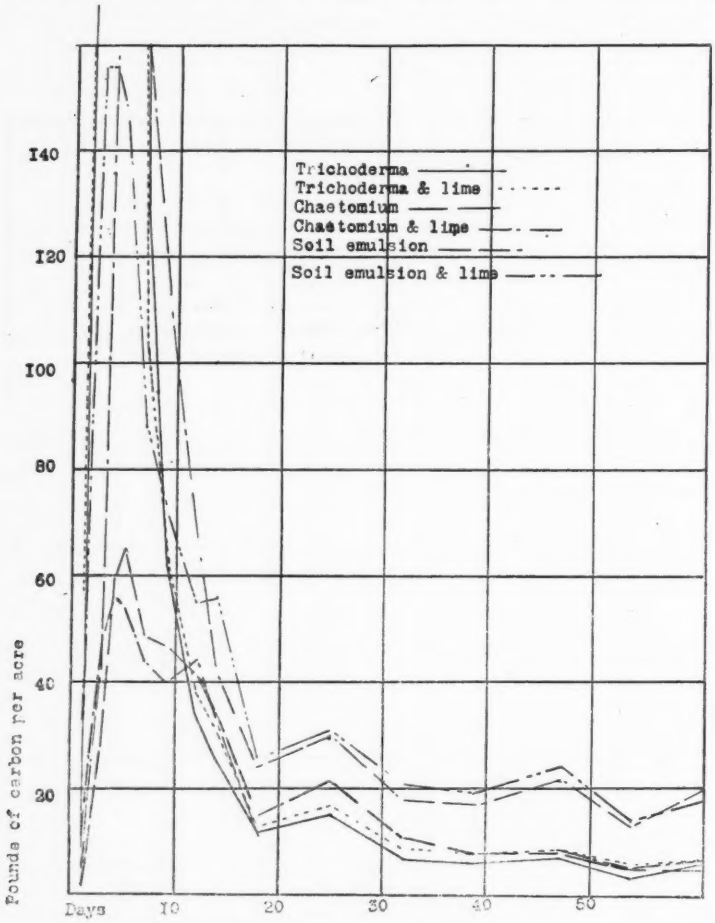

FIG. 4. DIAGRAM SHOWING OTHER AMOUNTS OF CARBON PRODUCED IN EXPERIMENT II

it is to be noted that almost invariably the unlimed soils have given more closely-agreeing duplicates than the limed. This might have been due to a difference in the amount of the lime decomposed by the heat treatment. Unfortunately, the soils were not analyzed for residual lime after the sterilization.

Keeping in mind the variations noted, it is seen that not much difference is to be noted in the amounts of carbon evolved from the limed and the unlimed soils. It is generally conceded that molds are more active in acid media than in neutral or alkaline media, yet this experiment does not seem to confirm it. The soil used had only a rather low lime requirement, so that possibly the hydrogen-ion concentration was not much different in the acid and in the limed soils. It is also seen that there is not much difference in the amount of carbon given from the limed and unlimed infusion-inoculated soils. In figures 3 and 4 the average daily results for the evolved carbon have been plotted. The course of the mold activity can be followed very easily by a study of these curves.

TABLE 4

Nitrate, ammonia and soluble non-protein nitrogen in the sterilized and unsterilized soil and in the sterilized inoculated soil after the completion of the experiment

NUMBER	TREATMENT	PER CENT OF TOTAL NITROGEN		
		Nitrate	Ammonia	Soluble non-protein
Original.....		0.325	0.60	14.45
Original.....	Sterilized.....	0.895	3.01	22.8
1, 2	Mucor.....	0.53	4.74	21.8
3, 4	Lime, Mucor.....	0.53	4.65	21.8
5, 6	Rhizopus.....	0.51	4.08	22.8
7, 8	Lime, Rhizopus.....	0.54	3.90	21.6
9, 10	Aspergillus.....	0.24	3.22	21.7
11, 12	Lime, Aspergillus.....	0.28	2.92	20.6
13, 14	Trichoderma.....	0.26	1.90	19.9
15, 16	Lime, Trichoderma.....	0.26	3.18	20.2
17, 18	Chætomium.....	0.46	4.64	21.9
19, 20	Lime, Chætomium.....	0.51	4.02	20.4
21, 22	Soil emulsion.....	0.61	5.30	19.6
23, 24	Lime, soil emulsion.....	4.52	2.08	14.9

The results for the determination of nitrate, ammonia, and non-protein nitrogen are given in table 4. Considering the results for nitrates, first, it is seen that in the mold-inoculated soils in every case, there is a diminution in nitrates, with the lime having no apparent effect. The soil-emulsion-inoculated and limed soils gave a considerable increase in nitrate nitrogen. There were some rather marked changes in the ammonia content of the soils. In only one case, that of the soil inoculated with *Trichoderma*, is there any considerable difference between the limed and unlimed soils, the latter having less ammonia than the limed soil. In the case of the soil-infusion-inoculated soils, no doubt the smaller amount of ammonia in the limed than in the unlimed soils is due to the greater nitrification in the former soils. The soluble non-protein nitrogen does not show any consistent changes except in case of the soil-emulsion-inoculated soils.

Experiment III

A different plan of sterilizing the soil was used in this experiment than in the preceding. It was thought that possibly sterilizing the soil with flowing steam in the Arnold sterilizer would be as effective as heating in the autoclave, and that less change would be brought about in the soil. In order to determine the number of times it was necessary to heat the soils in the Arnold sterilizer to bring about complete sterilization, the following preliminary experiment was carried out.

Several 500-cc. Florence flasks were prepared, each containing 1 pound of the air-dry soil, to which had been added 25 per cent of water, and then stoppered with cotton. It was found by experiment that it took about 40 minutes' heating in the sterilizer to bring the temperature in the center of the soil in the flask to that of boiling, namely, about 99°. Therefore, several of the flasks prepared as above were placed in the Arnold sterilizer, and heated for 1 hour and 40 minutes. This was repeated every alternate day until six heat treatments had been applied. Two of the flasks were then removed and allowed to stand at room temperature for one week, when the flasks were shaken, a few grams of the soil transferred to sterile water, and plates poured. Flasks receiving 7, 8 and 9 heat applications were treated in the same way with the following results:

6 treatments	5 contaminated plates, 3 sterile
7 treatments	1 contaminated plate, 7 sterile
8 treatments	No contaminated plate, 8 sterile
9 treatments	No contaminated plate, 9 sterile

It is seen that the soils heated 8 or 9 times in the sterilizer are undoubtedly sterile. Therefore, it was decided to heat the soils 9 times in the Arnold sterilizer. Twelve flasks were prepared, each containing 1 pound of the air-dry soil, and to six of these sufficient lime was added to give a treatment of 4 tons per acre. Twenty-five per cent of water was added, and rubber stoppers inserted bearing delivery tubes exactly as in the two preceding experiments. The flasks were then sterilized as indicated above.

Twelve of the flasks, of which six were limed, were then set up in much the same way as in the preceding experiment, except that the flasks were all placed in a water bath. It was originally planned to regulate the temperature, but after a few days, the mechanism failed. The water, however, served to keep the temperature of all the flasks alike. The inoculations were made as previously. The treatments, plating and carbon results are given in table 5.

It is seen that those flasks which had been inoculated with the *Rhizopus* were all contaminated with a *Penicillium* organism. The two unlimed soils were only slightly contaminated, while the two limed apparently were infected predominately with *Penicillium*. Although the inoculating cultures gave no indication of being impure, yet the conclusion seems rather clear that the

TABLE 5

Amount of carbon evolved as carbon dioxide from soils in Experiment III

(Results expressed as pounds per acre)

NO.	TREATMENT	REMARKS	DAYS AFTER STARTING			DAYS AFTER INOCULATION														TOTAL	AVERAGE
			1st	2–7	8	1	2	3	4–5	6–7	8–9	10–12	13–16	17–20	21–26	27–33	34–40	41–46	47–53		
1	Rhizopus nigricans	1–4	5	12	0	3	43	55	214	86	53	125	105	92	96	89	78	86	87	1,212	
2	Rhizopus nigricans	Contaminated with a Penicillium	5	8	0	3	49	72	236	78	53	113	107	88	90	85	66	82	84	1,206	1,209
3	Rhizopus nigricans, Lime	Contaminated with a Penicillium	34	133	32	47	53	60	125	99	57	lost		7							
4	Rhizopus nigricans, Lime	Contaminated with a Penicillium	31	100	27	48	52	55	115	77	50	106	97	78	53	68	43	55	66	963	963
5	Aspergillus niger	Pure at end	5	6	0	81	93	105	166	89	44	85	65	50	60	49	37	68	39	1,031	
6	Aspergillus niger	Pure at end	5	14	0	77	91	95	149	82	45	74	79	82	74	53	39	81	39	1,060	1,045
7	Aspergillus niger, Lime	Pure at end	34	120	32	127	91	66	83	66	39	78	82	75	60	63	56	114	118	1,118	1,118
9	Soil emulsion		4	10	0	3	27	79	322	220	113	161	224	162	97	79	67	83	58	1,695	
10	Soil emulsion,		5	10	0	3	8	23	266	230	142	193	180	134	118	90	75	126	124	1,712	7,103
11	Soil emulsion, Lime		40	230	46	70	85	81	156	111	74	181	151	133	134	106	78	88	84	1,532	1,532

noculum was the cause of the contamination. Soil 3 became contaminated on the ninth day, as a result of the stopper of the flasks coming out. Flasks 8 and 12 were broken during the course of the experiment.

The results for the carbon-dioxide determinations are not markedly different from those of the preceding experiment. Because of contamination, no conclusion can be drawn from soils 1 to 4. The limed soils inoculated with *Aspergillus niger* gave off more carbon dioxide than the unlimed, but unquestionably part of the increase was due to carbon dioxide in the soil water freed from the lime. This is indicated by the fact that considerable carbon dioxide was given from the limed soils before inoculation. Also, the excess carbon dioxide given from the limed soils at the end of the first day after inoculation must not

TABLE 6

Nitrate, ammonia and soluble non-protein nitrogen in the sterilized and unsterilized soils and in the sterilized inoculated soils after the completion of the experiment

NUMBER	TREATMENT	PER CENT OF TOTAL NITROGEN		
		Nitrate	Ammonia	Soluble non-protein
Original.....		0.325	0.60	14.45
Original.....	Sterilized.....	0.24	2.15	21.9
Original.....	Lime, sterilized.....	0.27	3.18	19.9
1, 2	Lime, sterilized.....	0.22	2.51	
4	Lime, sterilized.....	0.27	3.64	
5, 6	Lime, sterilized.....	0.21	2.17	
7	Lime, sterilized.....	0.22	4.04	
9, 10	Lime, sterilized.....	0.25	3.18	
11	Lime, sterilized.....	1.36	2.51	

have been due to increased organic activity, but rather to the carbon dioxide in the soil atmosphere and moisture. The limed soils, both the uninoculated and the inoculated, were analyzed for residual carbonate, but practically none was found. Therefore, the heat treatment caused all the calcium carbonate to be decomposed, and no doubt considerable excess carbon dioxide was left in the soil water and atmosphere.

In table 6 the nitrate, ammonia, and non-protein nitrogen results for the sterilized and unsterilized soils are given, together with the nitrate and ammonia results for the inoculated soils.

Comparing the results on the sterilized uninoculated soils given in table 6 with the corresponding results for the same soil in table 4, it is seen that the sterilizing in the Arnold sterilizer had but little less effect on the nitrogenous compounds than did autoclave treatment. The nitrate was considerably less changed, the ammonia not much different, nor was the soluble non-protein nitrogen changed to a much less extent. Evidently, the long continued treatment at the temperature of boiling has about the same effect as the shorter but higher temperature treatment in the autoclave. It is thought that possibly

complete sterilization could be effected by a considerably less number of treatments in the Arnold sterilizer than the nine to which we subjected our soils.

The results for the nitrate and ammonia nitrogen in the inoculated soils are about the same in a general way as those for the preceding experiment, and will not be discussed further.

SUMMARY AND CONCLUSIONS

The results of the experiments reported in this paper do not give a definite answer to the question as to whether molds are active in normal soils or not. Nevertheless, the fact that in some cases more, and in all cases nearly as much, carbon dioxide is evolved from sterilized soils inoculated with molds and from sterilized soils inoculated with soil emulsion, seems indicative that they may be. Of course, in sterilized soils conditions are quite different from those in normal soils. More plant-food and other materials are in a soluble state, a condition which is known to favor mold growth. However, it hardly seems probable that sterilization would change the soil from a medium absolutely unsuited to mold growth to a medium supporting molds to an extent equal or nearly equal to the support of the whole soil flora.

The definite conclusions to be drawn from this investigation are as follows:

1. Typical soil molds when inoculated into sterilized soil grow with a vigor equal to or nearly equal to the growth induced by an inoculation with the entire soil flora, the evolution of carbon dioxide being the measure of the vigor of growth.

2. Calcium carbonate in this soil causes no marked increase or decrease in the growth of molds as measured by the evolution of carbon dioxide.

3. Sterilization in the autoclave increased the nitrate, ammonia, and soluble non-protein nitrogen.

4. Sterilization in the Arnold sterilizer increased the ammonia and soluble non-protein nitrogen to a less extent than did sterilization in the autoclave. The amount of nitrate was decreased by treatment in the Arnold sterilizer.

5. Molds in all cases caused a diminution in the amount of nitrates. Ammonia was not much changed in amount. In nearly every case there was a decrease in the amounts of soluble non-protein nitrogen.

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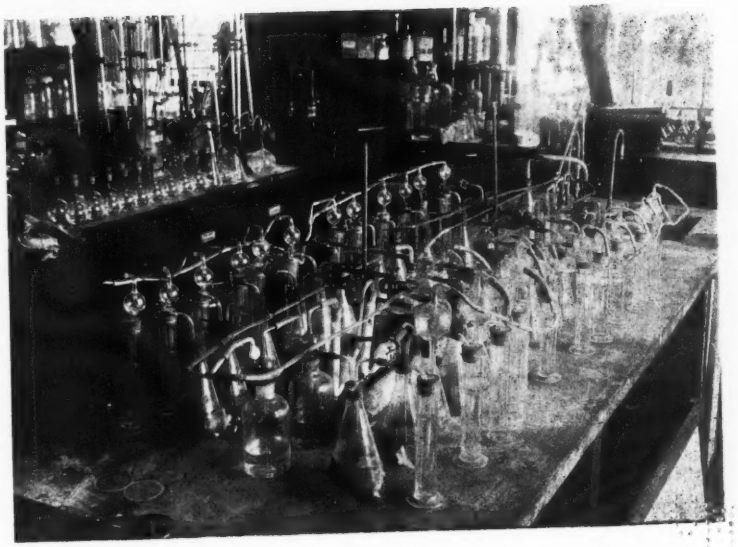
PLATE I

APPARATUS USED IN CONDUCTING EXPERIMENTS HERE REPORTED

PLATE I



THE CHEMICAL EFFECTS OF CaO AND $CaCO_3$ ON THE SOIL

PART I. THE EFFECT ON SOIL REACTION

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Received for publication April 4, 1918

The question of the chemical and physical effects on the soil of the different forms of lime has always been a subject of great interest to agricultural investigators. Innumerable field experiments have been carried out in order to determine how crops respond to the application of different forms and amounts of lime. In the majority of cases, however, no attempt has been made to discover the precise chemical changes induced in the soil system through the addition of lime. During the course of an extensive investigation on water extracts (1, 7), osmotic pressures (2), and reactions of soils (6), the suggestion was made that it would be of considerable interest to obtain further data concerning the effects of lime on the soil as evidenced by these methods of study. The present paper deals with the reaction of the soil, while the following article takes up the questions of water extracts and osmotic pressures.

Lime is applied to the soil either in the form of the oxide or carbonate. Sometimes one form is preferred, but often it is considered immaterial which is used, except as economic considerations may dictate. It is known that quicklime may sometimes have an injurious alkalinity soon after its application, but the assumption is generally made that carbonation quickly takes place, so that the ultimate effect is the same as though the carbonate had been used in the first place. It seemed profitable to study these changes with more exactitude, by using the hydrogen electrode method (6) for determining the concentration of H-ions in soil suspensions.

Three soils of different types were used, (1) a clay adobe, (2) a sandy loam, (3) a silty clay loam. A sample of beach sand was also included for comparison. Two 20-pound lots of each soil were placed in earthenware jars. Commercial quicklime was added to the soils and thoroughly mixed. The proportions used were 0.07 per cent and 0.28 per cent calculated in terms of pure CaO. The soils were made up to approximately an optimum moisture content and kept in this condition for six months. Samples were taken at intervals over this period and the H-ion concentration determined as described in the previous publication already cited (6). The samples were not dried and loss of CO_2 was avoided so far as possible in making the measurements. All determinations were carried out in a strictly comparable way. H-ion con-

TABLE 1

Effect of different forms of lime on soil reaction

NUMBER OF SOIL	DESCRIPTION OF SOIL	TREATMENT	P_H IMMEDIATELY AFTER TREATMENT	P_H AFTER 4 DAYS	P_H AFTER 7 DAYS	P_H AFTER 18 DAYS	P_H AFTER 26 DAYS	P_H AFTER 46 DAYS	P_H AFTER 80 DAYS	P_H AFTER 187 DAYS	P_H AFTER GROWING BARLEY 10 MONTHS AFTER TREATMENT	P_H SOIL + 0.10 PER CENT $CaCO_3$	P_H SOIL + 0.40 PER CENT $CaCO_3$
1	Clay adobe	None	7.56									7.39	7.39
1	Clay adobe	0.07 per cent CaO	8.56	8.36	8.56	8.00	8.50	8.05	8.74	8.00	8.22		
1	Clay adobe	0.28 per cent CaO.	10.16	9.26	9.43	9.08	8.74	8.94	9.00	8.70	8.84		
2	Sandy loam	None	7.56									7.87	7.80
2	Sandy loam	0.07 per cent CaO	9.26	8.18	8.50	8.05	8.25	8.11	8.56	8.29	7.87		
2	Sandy loam	0.28 per cent CaO	10.96	10.00	9.85	9.05	9.05	8.94	9.00	8.67	8.43		
3	Silty clay loam	None	7.77									7.80	7.81
3	Silty clay loam	0.07 per cent CaO	9.05	8.43	8.63	8.36	8.29	8.15	8.15	8.15	7.80		
3	Silty clay loam	0.28 per cent CaO	10.30	9.43	9.47	8.84	8.94	8.88	8.91	8.50	8.32		
4	Beach sand	None	7.35									8.08	8.18
4	Beach sand	0.07 per cent CaO	10.82	9.00	9.43	8.53	8.53	8.32	8.29	7.92			
4	Beach sand	0.28 per cent CaO.	12.45	11.68	11.51	10.89	10.65	9.61	9.05	8.39			

centrations are expressed as exponents, 7.10 being taken as neutrality, since it represents the H-ion concentration of pure water. The larger the exponent the greater is the intensity of alkalinity.

The results in table 1 indicate that immediately after the addition of CaO a very considerable increase in OH-ion concentration has been produced. With the larger application the increase is much greater than with the smaller quantity. Comparing the different soils, we find that the reaction of the clay adobe is least affected, while that of the sand undergoes the most marked change. Within three days there is a very great decrease in alkalinity in all cases. Thereafter the decrease is slower and six months later the treated soils still show an increased alkalinity due to CaO. The same soils when treated with equivalent or greater quantities of $CaCO_3$ do not have their reaction appreciably changed. All of the soils were slightly alkaline originally, but similar effects would probably be observed with acid soils, once an excess of CaO were added over that necessary to neutralize the acids present. In connection with the use of $CaCO_3$, Plummer (5) has recently shown that certain soils, to which a very large excess of $CaCO_3$ had been added, a number of years after treatment showed a decidedly high concentration of OH-ion. The carbonate seems to have reacted with the soil constituents, possibly forming silicates.

As a further test of the effect of CaO, a preliminary vegetation experiment was made with barley. Soils 1, 2 and 3 were used after contact with CaO for six months as previously indicated. After harvesting the crop the reaction of the soils was determined again and it was found that no significant change in the OH-ion concentration had occurred. The alkalinity was still greater than that of the untreated soil, but no inhibition of plant growth could be observed. In this connection it should be remembered that any excretion of CO_2 by the plant roots would tend to decrease the alkalinity, at least in the adjacent region.

In the course of another experiment two tanks of an acid fine sandy loam were treated with an excess of lime (about 0.5 per cent CaO), using on one lot CaO and on the other an equivalent quantity of $CaCO_3$. After standing out-of-doors for one year, samples were taken from both tanks and the H-ion concentration determined. The soil treated with $CaCO_3$ gave an exponent of 8.05, while that treated with CaO gave 11.34. The latter represents an intense alkalinity and it is clear that complete carbonation did not take place even after a long period of time. Several tests were made on the nitrifying power of the soil, 0.2 per cent $(NH_4)_2SO_4$ being used. The soil treated with $CaCO_3$ gave a nitrification of 100 per cent. In the case of the CaO-treated soil, no nitrification was observed after four weeks.

Hutchinson and MacLennan (3, 4) have made extensive studies of the effects of CaO and $CaCO_3$ in producing a partial sterilization of the soil. They found that $CaCO_3$ did not produce such sterilization but that CaO was capable of accomplishing this result. The quantity of lime required seemed to depend

upon the type of soil. These observations accord with the measurements of OH-ion concentration just described. In some soils there is considerable immediate chemical reaction between the CaO and some of the soil constituents, so that the OH-ion concentration may never be excessive unless a large percentage of CaO is used. On the other hand, even a small percentage in other soils may cause initially a very high concentration of OH-ions. The maximum effect is noted in sand. After the first few days the alkalinity decreases in all soils, either because of continued chemical action or of slow reaction with CO_2.

In summarizing the present experiments we may say that CaO when first added to a soil produces a high concentration of OH-ion. This decreases markedly within a few days and continues to decrease slowly over a considerable period, but the treated soils still show a greater intensity of alkalinity even after many months, as compared with the untreated soils or those treated with $CaCO_3$. When a considerable excess of CaO is used it is possible for certain soils to maintain such a high concentration of OH-ion that nitrification is practically inhibited. Thus the ultimate effects of CaO and $CaCO_3$ may not necessarily be identical. It is highly desirable that more exact observations be made of the reactions (H-ion concentration) produced by lime in order that its effects, chemical and biological, may be compared with the measurements of this important and definite factor.

SUMMARY

1. The hydrogen-ion concentration of several types of soil was determined after the addition of CaO and $CaCO_3$.

2. The initial effect of both low and high percentages of CaO was to greatly increase the OH-ion concentration. This decreases with time but is higher than in the case of the untreated soil even after ten months. These results are discussed with reference to bacterial activity and partial sterilization of the soil.

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THE CHEMICAL EFFECTS OF CaO AND $CaCO_3$ ON THE SOIL

PART II. THE EFFECT ON WATER-SOLUBLE NUTRIENTS IN SOILS

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Received for publication April 4, 1918

It is a well-known fact that the physical and biological conditions of soils are usually improved by the addition of calcium compounds. The preceding article by Hoagland and Christie (8) described the effect of different forms and amounts of lime on the reaction of typical soils. This paper shows that the initially high alkalinity produced by calcium oxide is rapidly reduced and that this effect is most pronounced in heavy soils. It seems probable, therefore, that this decrease in alkalinity is not entirely due to carbonation but at least in part to chemical reaction with the soil. In the case of calcium carbonate McIntire (11) states that when this compound is applied to soils in excess of the amount necessary for neutralization, the residual carbonate is gradually decreased, demonstrating "the existence of a long continued reaction between soils and carbonates."

The prevailing idea has been that lime compounds render certain other elements such as magnesium, potassium and phosphates more available, due to the phenomenon of interchange of bases. However, certain experiments seem to refute this theory. Lyon and Bizzell (9) found no increase of potassium in the drainage water or crops of limed soils, although magnesium was increased. The same authors in another paper (10) report the increase of soluble sulfates in limed soils. Bradley (3) found that gypsum acted as an indirect potassium fertilizer, while lime did not and that neither affected the water-soluble phosphates in soils. Briggs and Breazeale (4) have recently shown that pegmatite and orthoclase as well as soils containing these minerals do not yield increased water-soluble potassium when shaken with an aqueous solution of calcium hydrate or calcium sulfate. On the other hand, Andre (1) states that glauconite yields part of its potassium when treated with calcium carbonate. Morse and Curry (12) found that lime and gypsum increased the solubility of potassium in feldspar, claiming that this effect may not be observed when soils are similarly treated, owing to the removal of potassium from solution by the absorbent power of clay. Gaither (6) concludes that lime increases the availability of phosphates by replacement of iron and aluminum. He shows distinctly that silicates are decomposed but states that the assimilation of potassium by crops was decreased by caustic lime.

TABLE 1

Effects of CaO *and* $CaCO_3$ *on water extracts and osmotic pressures of soils*

		NO. 1 SANDY LOAM LEACHED	NO. 2 FINE SANDY LOAM STORED	NO. 3 FINE SANDY LOAM STORED	NO. 4 SILTY CLAY LOAM CROPPED	NO. 5 SILTY CLAY LOAM STORED	NO. 6A SILTY CLAY LOAM CROPPED	NO. 6B SAME AS 6A FALLOWED	NO. 7A CLAY ADOBE CROPPED	NO. 7B SAME AS 7A FALLOWED
Osmotic pressure (atm)	Untreated	0.43	4.94	3.13	0.59	1.93	0.78	5.06	0.69	1.46
		0.46	5.18	3.13	0.64	1.80	0.81	5.18	0.80	1.64
	$CaCO_3$	0.51	5.30	3.25	0.87	1.80		4.82	0.82	1.53
		0.49	5.42	3.25	0.75	1.80		5.18	0.75	1.69
	Average per cent increase	12	6	4	31	−3		−2	6	4
	CaO	0.59	5.30	3.37	0.83	1.93	1.05	5.18	1.06	1.53
		0.57	5.66	3.37	0.88	2.05	1.07	5.18	0.88	1.60
	Average per cent increase	29	8	7	39	6	33	1	32	
Total solids (p.p.m.)	Untreated	318	2332	1760	351	838	448	3788	598	1236
		285	2344	1756	369	809	461	3723	652	1359
	$CaCO_3$	342	2393	1870	475	803		3769	763	1352
		311	2346	1766	428	723		3795	753	1320
	Average per cent increase	8	1	4	26	−7		1	21	3
	CaO	371	2322	1885	428	996	559	3729	794	1335
		374	2322	1836	483	975	710	3801	786	1382
	Average per cent increase	23	−1	6	27	19	39		27	4
Calcium (p.p.m. Ca)	Untreated	32	352	174	33	93	53	396	42	135
		30	343	177	33	99	63	389	42	135
	$CaCO_3$	34	357	177	40	96		419	62	171
		38	354	177	33	93		413	81	164
	Average per cent increase	15	2	1	10	−1		6	70	24
	CaO	40	398	226	33	133	82	419	68	164
		35	404	220	36	133	85	440	71	167
	Average per cent increase	20	15	32	2	38	45	9	66	22

Magnesium (p.p.m. Mg)	Untreated	16	3.6	4.4	17	53	42	30	33	39
		16	3.8	4.5	17	54	42	29	32	36
	$CaCO_3$	17	3.7	4.7	27	47		36	33	38
		17	4.0	4.5	29	46		37	36	39
	Average per cent increase	5	5	2	66	−13		24	7	2
	CaO	19	3.7	4.4	31	47	40	38	38	39
		19	3.7	4.4	33	48	43	38	38	38
	Average per cent increase	16		−2	92	−11	−2	30	16	2
Potassium (p.p.m. K)	Untreated	24	53	128	20	65	38	123	44	59
		24	52	127	20	62	42	123	49	57
	$CaCO_3$	28	56	132	31	49		119	50	46
		29	60	124	32	52		123	49	48
	Average per cent increase	18	10		58	−21		−2	6	−19
	CaO	35	48	121	41	52	43	118	42	44
		37	50	110	38	51	41	121	44	48
	Average per cent increase	50	−5	−10	97	−19	7	−2	−8	−20
Phosphate (p.p.m. PO_4)	Untreated	7.9	7.0	39	5.8	22	7.9	3.3	13	7.3
		7.5	6.4	37	5.5	23	7.2	4.6	14	5.6
	$CaCO_3$	9.6	5.3	37	10.8	25		4.0	12	3.2
		9.6	7.0	38	11.4	23		4.0	10	2.2
	Average per cent increase	25	−7	−2	95	6			−18	−60
	CaO	9.0	8.2	33	10.1	22	7.2	4.6	11	7.1
		11.3	8.2	32	9.1	27	8.5	7.9	14	11.2
	Average per cent increase	33	22	−15	69	10	4	57	−3	40
Sulfate (p.p.m. SO_4)	Untreated	4.3	175	151	17	83	58	258	108	122
		5.4	180	147	19	86	57	247	107	119
	$CaCO_3$	28.7	171	146	27	84		302	125	115
		28.6	176	146	44	82		297	129	121
	Average per cent increase	485	−2	−2	44	−2		18	19	−3
	CaO	23.6	171	128	24	73	45	297	120	132
		23.6	197	142	24	70	47	288	120	130
	Average per cent increase	382	3	−9	35	−15	−20	15	12	9

TABLE 1—(Concluded)

		NO. 1 SANDY LOAM LEACHED	NO. 2 FINE SANDY LOAM STORED	NO. 3 FINE SANDY LOAD STORED	NO. 4 SILTY CLAY LOAM CROPPED	NO. 5 SILTY CLAY LOAM STORED	NO. A6 SILTY CLAY LOAM CROPPED	NO. 6B SAME AS 6A FALLOWED	NO. 7A CLAY ADOBE CROPPED	NO. 7B SAME AS 7A FALLOWED
Nitrate (p.p.m. NO_3)	Untreated	20	867	507	53	153	40	1036	12	319
		19	920	502	50	152	38	1035	12	340
	$CaCO_3$	20	901	524	52	159		1056	25	319
		21	866	530	54	152		1036	22	340
	Average per cent increase	3	−1	4	2	2		1	102	
	CaO	19	885	531	52	153	42	1076	16	324
		20	918	525	55	152	41	1058	12	329
	Average per cent increase		1	4	4		6	3	18	

It is evident from a consideration of these and other references that there is considerable divergence of opinion concerning the effect of calcium compounds on the available nutrients in soils. The purpose of the present paper is to discover possible reasons for this apparent disagreement between the several investigations on the important question of the indirect fertilizing action of lime compounds.

During an extensive investigation of the water extracts of soils carried on by this laboratory (5,13), the methods of analysis suitable for such extracts have been considerably improved and are believed to permit of more exact interpretation than was formerly the case. The present paper reports the data obtained from a study of the effects of calcium oxide and calcium carbonate on the concentration of the soil solution as measured by the water-extraction and freezing-point methods (2).

DESCRIPTION OF SOILS

None of the soils used in this investigation were acid and therefore no portion of the lime applied was used for neutralization. In table 1 is given the type and previous treatment of each soil. It should be noted that sandy loam no. 1, silty clay loams no. 4 and no. 6a and clay adobe no. 7a contained relatively low amounts of water-soluble nutrients, due in the case of the sandy loam to excessive leaching and in the others to the depletions caused by several seasons' cropping. The remaining soils which had been stored in bins or fallowed for several years showed a considerably greater accumulation of soluble plant-food. This is in accord with the recent findings of Stewart (13) who has shown that stored or fallowed soils show greater concentrations of all nutrients save phosphates than the same soil under crop. Soils 4, 5 and 6, although from different localities, are of the same series, Yolo silty clay loam, according to the soil surveys of the Bureau of Soils of the United States Department of Agriculture. This will be referred to later in connection with the different effects of lime on these soils.

PROCEDURE

Six 500-gm. portions of each air-dry soil were weighed into quart jars. To two jars of each soil was added 0.5 gm. C. P. $CaCO_3$ (equal to an application of 2 tons per acre-foot of 4,000,000 pounds), which was mixed with the soil before moistening. The next two jars were treated with 0.28 gm. C. P. CaO (equivalent in amount of calcium to the $CaCO_3$ application), added in a water suspension. This was found to be the most efficient method of mixing the oxide with the soil. The remaining two jars were not limed and served as controls. Certain investigators have used excessive quantities of lime in similar studies. In order to make the results of practical value, the amounts of lime here used are comparable with moderate field applications. After the addition of the calcium compounds, sufficient distilled water was added

to all jars to bring the soil to optimum, following which the contents of each jar were again stirred. All jars were then allowed to stand one week at ordinary temperatures, being loosely covered to prevent excessive evaporation, yet allowing easy access of air. At the end of seven days, the contents of each jar were removed and mixed. A 100-gm. portion was dried to constant weight to determine moisture. A 340-gm. sample was extracted with five times its weight of distilled water after the manner described by Stewart (13). The remainder was used to determine the osmotic pressure of the soil solution. This was done according to the method of Bouyoucos and McCool (2) which consists in determining the lowering of the freezing point directly in the soil under optimum moisture conditions.

Table 1 gives a complete résumé of the results obtained. The concentration of the soil solution is reported in atmospheres of osmotic pressure. The analyses of the soil extracts are reported as parts per million of water-free soil. Below each pair of duplicate determinations is shown the average per cent of increase or decrease resulting from the CaO and $CaCO_3$ additions.

DISCUSSION OF RESULTS

In any chemical study of soil fertility it is essential to determine the probable variation inherent in the methods used. For a complete discussion of the methods of extraction and analysis used in this investigation the reader is referred to the recent work of Stewart (13). For present purposes it is sufficient to state that the maximum variation between duplicate extractions of the same soil, for any element, was found to be 10 per cent and that the mean factor of error is approximately 3 per cent. The usual close agreement between duplicates shows that large variations are the exception rather than the rule. No conclusions should be drawn except where the increase or decrease due to lime is well above the average error.

Concentration of soil solution. Soils 1, 4, 6a and 7a show that the concentration of the soil solution has been materially increased by the addition of lime, the effect of CaO being more pronounced than that of $CaCO_3$. The remaining soils show little or no effect. It is interesting to note here that the soils showing increases are those recently cropped or having a low concentration, while those showing no effect contain a much greater concentration of nutrients due to fallowing or storage.

Total solids. Hoagland (7) has shown that although the 1:5 water extraction removes more material than is actually in the soil solution, there is a distinct correlation between these two values. In this connection it should be noted that the soils showing substantial increases of total solids on extraction are the same soils which show an increased concentration of the soil solution and the percentage increases are of approximately the same magnitude for both determinations.

Calcium. The increases in the case of calcium are quite variable, the CaO on the whole giving more soluble calcium than the $CaCO_3$. The manner in which the different soils react with lime compounds is reflected by the variable increases in water-soluble calcium.

Magnesium. The cropped soils, nos. 1, 4 and 7a, show increases in soluble magnesium. In the case of soil 6 this tendency is reversed, the fallowed soil giving an increase and the cropped soil none. Soil 4 shows approximately a 100 per cent increase in available magnesium which will be discussed later in connection with its possible effect on the lime-magnesia ratio. Soil 5 shows a distinct depression of soluble magnesium.

Potassium. Soils 1 and 4 unquestionably show large increases of available potassium due to both CaO and $CaCO_3$, CaO being the more potent. These two soils were the lowest in soluble potassium before treatment. The remaining soils show no increase, and in fact soils 5 and 7b experience a considerable depression of soluble potassium due to the lime. An inspection of the results obtained for this important element points out a probable reason for the disagreement between various investigators concerning the effect of lime as an indirect potash fertilizer.

Phosphate. Owing to the difficulty of obtaining closely agreeing duplicates in all cases, as well as to the small number of parts per million usually involved, no great confidence is felt in the results for this determination. However, soils 1 and 4 show marked increases in available phosphate for both CaO and $CaCO_3$ treatments, which increases are believed to be significant. The remaining data are not sufficiently in agreement to warrant discussion here. It might be conceived that the increased alkalinity due to lime may repress phosphate solubility but little or no evidence in favor of this theory is noticed here.

Sulfate The three cropped soils, nos. 1, 4 and 7a, and also 6b, produce increases in soluble sulfates. This is especially marked in soil 1 which shows an increase of approximately 400 per cent for both CaO and $CaCO_3$ treatments. The two soils showing the greatest increases are those lowest in soluble sulfates.

Nitrates. With the single exception of soil 7a, no soils show significant increases in nitrates. The small absolute increase of nitrates in this soil produces a large percentage increase, because of the low amount of nitrates resulting from crop depletion. It will be remembered that these soils had been allowed to stand only one week at ordinary temperatures. If nitrification may be taken as a partial index of bacterial activity in the soil, then the observed effects of lime on these soils must be due to a purely chemical reaction and not to any stimulation of the biological agencies in the soil.

GENERAL DISCUSSION

In order to demonstrate more conclusively the direct chemical effect of the lime, another sample of soil 4 was treated with 0.4 per cent CaO (8 tons per

acre-foot) and allowed to stand only 24 hours before analysis. The following results unquestionably show the immediate chemical effect of the quicklime.

	Total solids.	Ca	Mg	K	PO_4	NO_3
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
Limed	274	34	13	32	5	19
Not limed	505	64	23	46	9	14

Larger portions of soils 1, 4 and 7a, in gallon crocks, after being treated with CaO and $CaCO_3$, were planted to barley. The yield of barley in the limed soils reflected the beneficial effects of the calcium, being from two to three times greater than the controls. This increased yield may be largely accounted for by improved physical and biological conditions. Without giving the detailed figures, it may be stated that the analyses of the soils before planting showed marked increases in total solids, calcium, magnesium and potassium, and it is believed that these increases in available nutrients must account, at least in part, for the increased crop.

It is a well-known fact that lime decomposes organic matter in soils and therefore it might well be contended that the increases in total solids were largely due to soluble organic matter. In the case of about half the soils examined, the electrical conductivity of the soil extract was measured. The figures obtained were in direct relation to the total solids determination, showing that at least the greater part of the increases were due to inorganic and not to organic matter.

Certain other inorganic elements, such as sodium, silicon, etc., have not been determined. Where increases in the nutritive elements do not account for the total increase in total solids, it is probable that such other undetermined elements have been made more soluble. Gaither (6) has previously shown the decomposition of silicates in soils by lime. It would be perfectly reasonable to assume that other elements such as silicon and sodium have been rendered more soluble in some of the soils.

Soils 5 and 6b are of the same type and series and yet react with lime in different fashion. This indicates that the changes induced by liming are more deep-seated than can be accounted for by soil classification.

Lyon and Bizzell (9) found in a certain soil that the addition of lime caused a narrower lime-magnesia ratio in the drainage water. If there is any value in a certain lime-magnesia ratio for soils, it must be concerned with the water-soluble elements. An inspection of the figures for calcium and magnesium in soil 4 shows that while the original soil had a lime-magnesia ratio of 2:1, after liming the ratio became 1:1, as a result of the liberation of magnesium by the calcium. Certain of the other soils produced a broader ratio due to increases in calcium or depressions in magnesium, or both. It is seen from this that the calcium-magnesium ratio of a soil solution cannot be predicted prior to the addition of lime.

It is evident from the data considered that all soils do not react chemically with lime in the same manner. Furthermore, even the same soil under different concentrations of soil solution, due to cropping or fallowing, may react differently. No attempt is made to explain the reasons for the changes observed. Evidently, the addition of lime compounds changes the equilibrium in the complex soil solution and the resultant effects are varied and impossible to predict. Further study involving determinations of all the elements concerned would be necessary before even a plausible hypothesis could be advanced.

SUMMARY

1. The direct chemical effects of CaO and $CaCO_3$ on the water-soluble nutrients in 7 soils of 3 different types have been studied. Supplementary data by freezing-point and conductivity methods have been obtained.

2. CaO and $CaCO_3$ increased the water-soluble potassium in only 2 soils, and in 2 soils caused a depression. Soluble magnesium was increased in 4 soils, and decreased in 1 case. Soluble sulfates were increased in 4 soils. Only 2 soils showed a significant increase in phosphates.

The effects of CaO are more pronounced than those of $CaCO_3$.

3. The effect of lime on soils depends in part upon the previous treatment of the soil, particularly with respect to the concentration of the soil solution. A greater effect was observed in soils having a low initial concentration.

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THE RELATIVE "RAWNESS" OF SOME HUMID SUBSOILS[1]

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Received for publication March 5, 1918

INTRODUCTION

Three recent articles (1, 2, 4) dealing with the relative "rawness," or unproductivity, of subsoils as compared with surface soils make it appear that the prevailing views upon the subject rest upon an uncertain foundation. The unproductivity of the subsoils of humid regions has long been recognized, as Alway, McDole and Rost (2, p. 9–10) have pointed out, and no distinction has been made between non-leguminous plants and inoculated legumes. On the contrary, the subsoils of arid regions have been regarded as characterized by a lack of any such rawness, Hilgard's views upon these having been accepted without question.

Alway, McDole and Rost presented evidence from both pot experiments and field observations in support of the view that certain humid subsoils, viz., those developed on the loess of eastern Nebraska, with inoculated legumes are practically as productive as the corresponding surface soils, although very unproductive with non-leguminous plants.

Lipman (4) denies the correctness of Hilgard's views upon the rawness of arid subsoils in so far as these concern non-legumes, and concludes from his own observations in California that the subsoils of arid regions are practically as raw toward such plants as are the typical subsoils of humid regions. He further questions the actual existence of any proof of the rawness of humid subsoils toward legumes, or, as he puts it, whether legumes will not grow on these. But, as Alway has emphasized (1, p. 197), the question of rawness depends not upon whether the plants will merely *grow* but upon whether they will *thrive*, or make a growth at all comparable with that on the corresponding surface soils.

The experiments described below, undertaken at the suggestion of Dr. F. J Alway and carried out as subsidiary to a chemical study of prairie soils in comparison with those still covered with virgin forest, furnish evidence of as great a productivity in the case of some of the forest subsoils as that of the subsoils of the prairie-covered loess reported by Alway, McDole and Rost, while the corresponding prairie subsoils, with fewer of the characteristics typical

[1] Published with the approval of the Director as Paper No. 113, of the Journal Series of the Minnesota Agricultural Experiment Station.

of those of humid regions, were found to be decidedly unproductive. As the author's work on the subject has now been interrupted for an indefinite period the data so far accumulated are presented below.

PROPERTIES OF THE SOILS

The location of the fields from which the soils were secured and the differences in precipitation and natural vegetation are shown in figure 1. In the case of

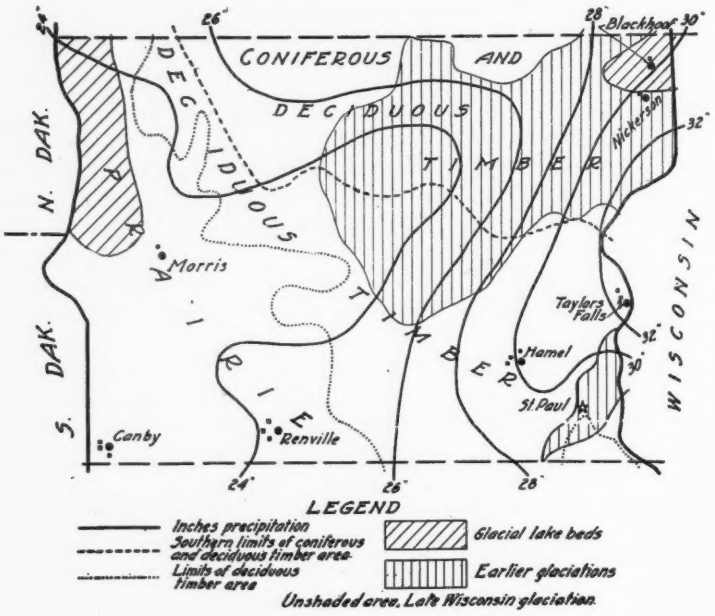

FIG. 1. MAP OF PORTION OF MINNESOTA

Showing sources of soils used, boundaries of the Late Wisconsin glaciation (after Leverett, 3, p. 32), normal precipitation (after Purssell, 3, p. 22), and distribution of forest and prairie (after Upham and Butters, 3, p. 39).

all except those from Blackhoof and Nickerson, both surface soil and subsoil consist of till from the Late Wisconsin glaciation. The Blackhoof soils are of lacustral origin, having been deposited in glacial Lake Duluth (3, p. 32) and the Nickerson samples are from a very sandy moraine at the edge of this lake. Accordingly, all except those from Nickerson are products of the very latest continental ice sheet and so have been exposed to the action of the weather and of vegetation for approximately the same length of time.

In table 1 are indicated the important properties of the different soils used in the vegetation experiments. The organic carbon was determined by com-

bustion with copper oxide in a current of oxygen. The degree of acidity reported is that found by the Truog method. Effervescence was tested by treating the thoroughly moist sample with 10 per cent hydrochloric acid. It will be seen that in the case of a few soils the reaction became less acid during the course of the experiment, as the result of the use of tap water which con-

TABLE 1

Composition and properties of the soils used

LOCALITY	DEPTH	MOISTURE EQUIVALENT	NITROGEN	ORGANIC CARBON	ORGANIC MATTER*	REACTION OF SOIL		EFFERVESCENCE WITH HCl
						At beginning	At conclusion	
			per cent	*per cent*	*per cent*			
Canby.....	1 to 6 in.	30.25	0.329	4.015	6.922	Neutral	Neutral	None
	3rd ft.	23.24	0.051	0.770	1.328	Neutral	Neutral	Strong
Morris.....	1 to 6 in.	30.46	0.330	4.444	7.662	Neutral	Neutral	None
	1st ft.	27.78	0.280	3.303	5.695	Neutral	Neutral	None
	3rd ft.	18.16	0.042	0.642	1.107	Neutral	Neutral	Strong
	5th ft.	17.39	0.013	0.244	0.421	Neutral	Neutral	Strong
Renville...	1 to 6 in.	35.91	0.393	5.134	8.852	Neutral	Neutral	None
	3rd ft.	27.28	0.051	0.865	1.491	Neutral	Neutral	Strong
Hamel.....	1 to 6 in.	23.02	0.181	2.405	4.146	Slightly acid	Very slightly acid	None
	3rd ft.	26.72	0.048	0.390	0.672	Neutral	Neutral	Very slight
Taylors Falls.	1 to 6 in.	19.47	0.152	1.900	3.276	Slightly acid	Slightly acid	None
	3rd ft.	18.12	0.029	0.248	0.428	Slightly acid	Neutral	None
Blackhoof	1 to 6 in.	35.13	0.188	2.732	4.710	Medium acid	Medium acid	None
	3rd ft.	41.91	0.026	0.295	0.509	Neutral	Neutral	Strong
	5th ft.	52.50	0.022	0.345	0.595	Neutral	Neutral	Strong
Nickerson	1 to 6 in.	6.95	0.068	0.951	1.640	Strongly acid	Medium acid	None
	3rd ft.	1.56	0.006	0.094	0.162	Very slightly acid	Neutral	None

* Computed from organic carbon. Organic matter = C x 1.724

tained a considerable amount of calcium bicarbonate. As a single-valued expression of the texture the moisture equivalent is reported.

Three sets of soils, those from Morris, Blackhoof and Nickerson, were taken from a single field each. The samples from Morris were composites from 20 pits 2 rods or more apart, and those from Blackhoof from 3 pits 5 rods apart, while those from Nickerson were from 10 pits 16 rods or more apart. The sets from the four other localities were each composites from 3 fields, 2

miles or more apart. In each of these latter fields, composite samples were prepared from 5 pits 2 rods or more apart; the same volume of soil from each pit was used in making the field composites and the same weight of each of these field composites in making the area composites used in the vegetation experiments.

None of the fields had ever been brought under the plow, those at Canby, Renville and Morris being prairie fields used as meadows, while those at Hamel and Taylors Falls formed remnants of the original deciduous forest, few trees having been cut and no sign of injury by fire being found. The original forest of red and jack pine at Nickerson and of white pine at Blackhoof had been cut off by the lumbermen and both areas had, some twenty-four years ago, been burned over by severe forest fires. A young growth, chiefly deciduous, had since sprung up.

The bulk soils after reaching the laboratory were exposed to the air long enough to make them almost air-dry, then thoroughly mixed and tamped into the vegetation vessels.

EXPERIMENT I. SOILS FROM THREE LEVELS

In the first experiment, 1915–1916, soils from only Morris and Blackhoof were employed, each being represented by three samples, viz., the surface 6 inches and the third and fifth feet from the latter and the first, third and fifth feet from the former. Wooden boxes, 12 inches square and 8 inches deep, coated on the inside with pitch tar and provided with holes in the bottom for drainage, were employed as vegetation vessels. Four were filled from each sample. The soil was thoroughly moistened and at once planted to corn, but, at the end of two weeks, and before the plants had begun to show any distinct differences, the corn was removed, two of the boxes planted to barley and the other two to alfalfa. All the soils were kept well moistened with tap water.

The barley, early thinned to 12 plants per box, made a normal growth on the surface soil, producing well filled heads, but that on the subsoil was stunted, yellowish-green in color and formed very little seed. The alfalfa, at the end of about two weeks was thinned to 18 plants per box and treated with a suspension prepared by macerating nodule-bearing alfalfa roots in water. A second application insured the inoculation of all the plants, as indicated by their dark green color. Three crops were harvested. The appearance of the plants (plate 1) and the yields (table 2) indicate that the subsoils from both places were quite raw, being practically as unproductive of alfalfa as of barley. The latter was not cut until it was thoroughly ripe, but before the total dry weight and the weights of grain had been determined the plants were accidentally destroyed. The heads of the plants from the subsoils contained very few seeds, thus making the differences between the surface soil and subsoil crops much greater than the number of heads would indicate.

EXPERIMENT II. SOILS FROM TWO LEVELS

In the second experiment only two depths were represented, the surface 6 inches and the third foot. Fresh material from Blackhoof and Morris was employed along with recently collected samples from the other places. The soils, prepared as in the first experiment, were placed in galvanized iron pots, 12 inches deep, with a surface area of 0.75 square foot, and painted on the inside with pitch tar. Drainage was effected by holes in the bottom and a

TABLE 2

Yields of crops in first experiment

SOIL	POT NO.	ALFALFA (DRY MATTER)				BARLEY				
		First crop June 12	Second crop July 19	Third crop Sept. 30	Total 3 crops	Green weight	No. of culms	No. of plants	Average height of plants	No. of heads
Prairie soil from Morris										
		gm.	*gm.*	*gm.*	*gm.*	*gm.*			*inches*	
First foot	1	21.4	13.1	13.4	47.9	72.7	28	12	32.0	21
	2	20.0	15.5	14.0	49.5	67.0	23	11	33.0	15
Average		20.7	14.3	13.7	48.7	69.8	25	11	32.5	18
Third foot	1	3.8	4.0	5.7	13.5	18.3	10	10	19.5	8
	2	4.0	5.1	6.3	15.4	17.0	11	11	19.0	7
Average		3.9	4.5	6.0	14.4	17.6	10	10	19.2	7
Fifth foot	1	1.8	1.7	2.4	5.9	8.3	9	9	16.0	7
	2	2.2	2.4	2.3	6.9	9.5	12	11	15.0	5
Average		2.0	2.0	2.3	6.4	8.9	10	10	15.5	6
Forest soil from Blackhoof										
1 to 6 inches	1	27.8	28.4	19.0	75.2	92.0	41	11	32.0	21
	2	33.1	36.6	23.9	93.6	112.0	38	10	33.0	15
Average		30.4	32.5	21.4	84.4	102.0	40	10	32.5	18
Third foot	1	3.8	3.5	2.6	9.9	12.0	10	10	19.5	8
	2	2.5	2.1	1.8	6.4	10.0	11	10	19.0	7
Average		3.1	2.8	2.2	8.1	11.0	10	10	19.2	7
Fifth foot	1	2.8	2.2	1.6	6.6	9.5	12	12	16.0	7
	2	3.0	2.7	1.6	7.3	9.0	11	12	15.0	5
Average		2.9	2.4	1.6	6.9	9.2	11	12	15.5	6

half-inch layer of coarse gravel. In this experiment, instead of sowing seed, the writer transplanted 10 alfalfa plants secured from a field sown 5 months before, care being taken to select roots of uniform size. As only plants with adhering nodules were employed it appeared unnecessary to take any further measure to insure inoculation and none of the plants at any subsequent time gave evidence of lack of inoculation. The soil was moistened, the roots spread

TABLE 3

Yields of dry matter from four crops of alfalfa, number of plants surviving and weight of roots

SOIL	POT NO.	YIELD OF DRY MATTER						NUMBER OF SURVIVING PLANTS	WEIGHT OF ROOTS	WEIGHT OF SOIL PER POT
		Preliminary crop December 19, 1917	First crop May 14, 1917	Second crop June 25, 1917	Third crop August 18, 1917	Fourth crop October 3, 1917	Total for 4 crops			
Canby										
		gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*		*gm.*	*kgm.*
1 to 6 inches	1	8.3	10.7	14.4	19.4	6.5	51.0	8	31	14.9
	2	4.9	12.3	15.5	18.0	6.9	52.7	6	24	14.9
Average		6.6	11.5	14.9	18.7	6.7	51.8	7	27.5	
Third foot	1	6.8	6.4	5.5	5.7	0.5	18.1	10	31	22.0
	2	5.5	4.6	7.9	8.1	1.0	21.6	9	29	22.0
Average		6.1	5.5	6.7	6.9	0.7	19.8	9.5	30	
Morris										
1 to 6 inches	1	3.4	20.0	19.9	26.9	16.2	83.0	6	35	18.8
	2	8.6	18.7	18.3	31.2	17.6	85.8	6	39	18.8
Average		6.0	19.3	19.1	29.0	16.9	84.4	6	37	
Third foot	1	6.5	7.7	6.3	7.5	2.0	23.5	6	25	22.8
	2	6.5	7.4	7.1	7.3	2.0	23.8	6	24	22.8
Average		6.5	7.5	6.7	7.4	2.0	23.6	6	24.5	
Renville										
1 to 6 inches	1	7.7	14.8	15.2	27.3	13.3	70.6	9	41	16.7
	2	8.0	13.8	14.0	27.8	14.5	70.1	7	37	16.7
Average		7.8	14.3	14.6	27.5	13.9	70.3	8	39	
Third foot	1	8.0	3.0	6.7	3.8	0.6	14.1	8	28	21.1
	2	4.6	4.8	6.8	4.2	0.7	16.5	9	20	21.1
Average		6.3	3.9	6.7	4.0	0.6	15.3	8.5	24	
Hamel										
1 to 6 inches	1	4.9	20.8	22.4	25.9	15.4	84.5	7	39	20.5
	2	5.1	19.1	19.3	24.7	12.3	75.4	2	26	20.5
Average		5.0	19.9	20.8	25.3	13.8	79.9	4.5	32.5	
Third foot	1	8.1	16.9	19.0	22.9	12.7	71.5	10	42	21.4
	2	6.6	21.7	20.3	22.9	16.0	80.9	7	36	21.4
Average		7.3	19.3	19.6	22.9	14.3	76.2	8.5	39	

TABLE 3—Continued

SOIL	POT NO.	YIELD OF DRY MATTER						NUMBER OF SURVIVING PLANTS	WEIGHT OF ROOTS	WEIGHT OF SOIL PER POT
		Preliminary crop December 19, 1917	First crop May 14, 1917	Second crop June 25, 1917	Third crop August 18, 1917	Fourth crop October 3, 1917	Total for 4 crops			
Taylors Falls										
		gm.	*gm.*	*gm.*	*gm.*	*gm.*	*gm.*		*gm.*	*kgm.*
1 to 6 inches	1	4.6	20.9	17.0	20.2	13.5	71.6	6	37	21.9
	2	7.0	22.5	18.5	24.6	14.1	79.7	7	41	21.9
Average		5.8	21.7	17.7	22.4	13.8	75.6	6.5	39	
Third foot	1	6.8	24.5	20.5	21.9	15.2	82.1	10	36	22.4
	2	6.3	20.0	18.3	25.6	14.8	78.7	10	38	22.4
Average		6.5	22.2	19.4	23.7	15.0	80.4	10	37	
Blackhoof										
1 to 6 inches	1	6.9	24.1	19.4	32.0	19.2	94.7	7	48	19.0
	2	7.2	25.2	26.8	32.9	22.2	107.1	4	43	19.0
Average		7.0	24.6	23.1	32.4	20.7	100.9	5.5	45.5	
Third foot	1	6.6	2.4	6.1	4.7	1.1	14.3	9	18	18.6
	2	6.0	4.9	6.0	7.2	2.2	20.3	6	20	18.6
Average		6.3	3.6	6.0	5.9	1.6	17.3	7.5	19	
Nickerson										
1 to 6 inches	1	5.9	24.5	17.3	21.8	13.3	76.9	5	37	22.9
	2	4.3	28.4	23.3	19.2	11.9	82.8	3	25	22.9
Average		5.1	26.4	20.3	20.5	12.6	79.8	4	31	
Third foot	1	6.6	13.7	10.3	12.5	5.1	41.6	6	28	26.8
	2	5.4	12.7	12.2	13.3	5.7	43.9	10	28	26.8
Average		6.0	13.2	11.2	12.9	5.4	42.7	8	28	

out as much as possible, the soil pressed firmly about them and more water at once added. By the use of this method it was hoped that a crop would be obtainable in a shorter time and it also promised to assure the penetration of the fine-textured subsoils by the roots, which it was suspected might have partly caused the poor yields of alfalfa in the first experiment.

The transplanting was done on November 12, 1916, and the first crop developed very rapidly during the following two weeks, doubtless as a result of the supply of nutrients in the transplanted roots. At the end of five weeks, on December 19, the growth had practically ceased, and the tops were removed, a remarkably uniform yield from all the soils being shown (table 3). After this first, or preliminary crop, the plants made little growth for several months, the next cutting being secured on May 14. Three additional crops

were obtained, harvested on July 25, August 18 and October 3. The preliminary crop is not included in the total yields, as this is not to be attributed to nutrients derived from the respective soils. After harvesting the last crop the roots were carefully removed from the pots, washed to free them from adhering soil, dried and weighed. In all pots the roots were well scattered throughout the soil mass, penetrating to the bottom and into the washed gravel placed there to facilitate drainage.

The yields from the duplicate pots were very similar, in fact so nearly alike both in the different crops and in the total for all four that the use of single pots of each soil would have led to exactly the same conclusions as to their relative productivity. The content of nitrogen and that of organic matter in the productive subsoils from the forest fields were rather lower than those of the prairie subsoils which proved raw.

TABLE 4

Dry matter in the tops from four crops of alfalfa and in the roots at the end of the experiments

SOIL	TOPS		PRODUCTIVITY OF SUBSOIL	ROOTS		RATIO OF TOPS TO ROOTS	
	Surface	Subsoil	Yield on surface soil = 100	Surface	Subsoil	Surface	Subsoil
	gm.	*gm.*		*gm.*	*gm.*		
Canby	51.8	19.8	38	27.5	30.0	1.9	0.7
Morris	84.4	23.6	28	37.0	24.5	2.3	1.0
Renville	70.3	15.3	22	39.0	24.0	1.8	0.6
Hamel	79.9	76.2	95	32.5	39.0	2.5	2.0
Taylors Falls	75.6	80.4	106	39.0	37.0	1.9	2.2
Blackhoof	100.9	17.3	17	45.5	19.0	2.2	0.9
Nickerson	79.8	42.7	54	31.0	28.0	2.6	1.5

In four of the seven sets, those from Morris, Canby, Renville and Blackhoof, the yield on the subsoil was only from one-sixth to two-fifths of that on the corresponding surface soil (table 4). In the Nickerson set the yield on the subsoil was slightly more than half that on the surface material. In the case of the forest-covered fields at Hamel and Taylors Falls the subsoils yielded as well as the corresponding surface soils. Four of the seven subsoils, those from Morris, Canby, Renville and Blackhoof, were very rich in carbonates, all showing a strong effervescence with hydrochloric acid. The fields at the first three places were prairies and the rainfall at all three is lighter than at Hamel or Taylors Falls where the subsoils showed little carbonate.

From table 3 it will be seen that while the number of surviving plants varied from 2 to 10 per pot, the weight of the roots varied but little. Where only a few plants had survived the roots of these showed a much greater development than where few or no plants had died. That this variation in the number of surviving plants exerted no distinct influence upon the yield of alfalfa may be seen by comparing the yields from the duplicate pots, those from Hamel and Blackhoof furnishing especially good illustrations.

The fact that in the case of the four surface soils corresponding to the unproductive subsoils the yields of alfalfa vary with the weight of the soil in the pots, would suggest that the amount of soil to which the roots had access had a much greater influence upon the yields than did the number of plants.

SUMMARY

Alfalfa was grown in the greenhouse on seven sets of Minnesota glacial soils, each set consisting of the surface 6 or 12 inches of virgin soil and the corresponding subsoil taken from the third foot. Three sets were secured from prairie fields with a very calcareous subsoil and the others from forested areas. Two of the subsoils, both low in carbonates and from forest fields, yielded as well as both the corresponding and the other surface soils, while the five other subsoils gave yields only from one-sixth to one-half as high as the corresponding surface soils. The nitrogen content of the productive subsoils was no higher than that of those which proved "raw."

Thus, in the humid state of Minnesota, some of the glacial subsoils are as productive of alfalfa as surface soils when inoculation is assured, but others are quite unproductive, and the rawness is not associated with an especially low nitrogen content or with a lack of carbonates.

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PLATE 1

Alfalfa and barley on soil from the different foot levels (first, third and fifth), showing the unproductivity of the subsoils toward both crops. In the Blackhoof set the surface sample was from only the first half-foot section.

2
1
BLACKHOOF
1
3
5
MORRIS
1
3
5
2
1
BLACKHOOF
1
3
5
MORRIS
1
3
5

CHEMICAL CRITERIA, CROP PRODUCTION AND PHYSICAL CLASSIFICATION IN TWO SOIL CLASSES

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Received for publication April 22, 1918

Several publications (1, 3, 7) were recently issued from this laboratory embodying the results of an extended series of studies of soils in the cropped and the uncropped condition. The general conclusion presented in these articles was that there is a much closer relationship between the soil solution and water extracts of soils than is commonly supposed. The studies referred to also included a comparison of the results of analysis of all of our soils by the complete (fusion method) hydrochloric acid (sp. gr. 1.115) and citric acid (1 per cent) extraction methods. These latter results were not published inasmuch as they showed little or no relation to crop production and served only to fix our long held conviction that the first two methods at least are absolutely worthless as criteria of the present productivity of soils. Since our work on water extractions appeared, however, we have received a number of requests for information as to the other chemical characteristics of our soils. It therefore seems desirable to publish these latter in order that others may be able to draw their own conclusions as to the relative value of the various methods.

We have been unable to avoid the conclusion that in spite of inconclusive or negative results in the application of the various methods referred to, many workers continue to draw inferences from data obtained by their use as to the fertility of soils at present or in the near future. One of these methods is also frequently used for classifying soils with reference to their probable endurance. Results obtained by all methods are perhaps applicable to a discussion of the relation between chemical composition and physical texture. Our data seem to lead to certain conclusions with reference to all of these points and thus further justify their publication.

The origin, physical composition, behavior under crop, periodic results of water extractions and much other data concerning the soils discussed in this article are described elsewhere (7) in great detail. We shall limit our descriptions here to the mechanical analyses, but use such designating numbers and expressions as will enable the reader to refer readily to the article cited.

The soils used were all selected with reference to the United States Bureau of Soils classification. They comprised 5 silty clay loam soils of a single series and 8 fine sandy loams of different series. Our objective in selecting these soils was to obtain one group of as nearly identical physical texture and origin

as possible and another group which should belong to an identical class but differ in that the individual representatives belong to different soil series. The presence of the single clay loam is due to an erroneous preliminary physical classification. It is so very similar in its chemical properties to the silty clay loams that for most purposes we have grouped it with these latter. All soils have been cropped and under continuous observation for three years. They are kept in tight containers 30 by 60 inches in area, 18 inches deep, and watered with distilled water.

TABLE A

Mechanical Analysis. (Averages of two analyses)

CLASS	SILTY CLAY LOAMS						FINE SANDY LOAM							
Series	Yolo						Hanford	Fresno	Kimball	Tejunga	Madera	Arnold	Unnamed	Standish
Soil No.	1	2	3	4	5	6*	7	8	9	10	11	12	13	14
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Fine gravel (1–2 mm.)....	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.016	0.00	0.00	0.00	0.04	0.00
Coarse sand (1–1.5 mm.)	0.15	0.60	0.60	2.09	1.84	0.746	2.82	1.95	9.986	1.57	2.77	4.99	7.77	3.09
Medium sand (0.5–0.25 mm.)	0.23	1.50	1.04	1.24	1.70	0.574	2.87	3.19	6.308	2.94	2.818	4.38	14.55	4.05
Fine sand (0.25–0.010 mm.)...	1.69	8.00	3.53	5.47	9.61	1.786	15.60	21.22	21.730	16.62	20.945	23.27	13.49	24.54
Very fine sand (0.01–0.05 mm.)	32.62	31.26	26.28	30.32	32.73	21.775	53.67	50.63	43.67	38.76	39.34	46.24	15.70	38.94
Silt (0.05–0.005 mm.).....	42.68	36.97	38.12	37.99	30.52	37.415	16.01	17.57	10.87	26.25	19.075	9.61	34.72	15.55
Clay (0.005–0 mm.).....	24.17	22.47	28.47	25.08	24.72	39.380	9.77	5.56	8.19	13.37	14.62	9.44	12.95	13.87
Sum of percentages.....	101.54	100.80	98.68	102.19	101.12	101.676	100.58	100.12	100.77	99.51	99.568	97.93	99.22	100.04
Gravel removed by previous screening.....	0.11	0.09	0.39	6.15	3.38	0.11	3.64	0.99	6.41	0.59	2.12	1.57	1.15	2.21

* Clay loam.

TIME OF EXAMINATION OF SOILS

The complete analyses and those of the extracts obtained by hydrochloric and citric acid were made only once and at the commencement of our experiments. The results by water extractions, however, varied from day to day and were very low with soils under crop at the height of the growing season. It is evident that determinations at no single date could represent the potential fertility of a soil. The data on water extractions are therefore the averages of the results of periodic examinations of uncropped soils in the year 1916 when the soils had been in place for an entire calendar year and had had every opportunity to come into equilibrium with their local environment.

FORM OF REPORTING RESULTS

Analyses of the hydrochloric and citric acid extracts are usually reported in the conventional forms: potash (K_2O), lime (CaO), magnesia (MgO) and phosphoric acid (P_2O_5), etc. Complete analyses are sometimes reported as the elements and sometimes in the conventional forms. Water extractions are usually reported in terms of parts per million of the various ions. For purposes of comparison of the different methods it is deemed desirable to report all results in terms of the conventional forms. Results by the first three methods are expressed as percentages, but those from the water extractions will be expressed as parts per million, since the conversion of these to percentages seems to subserve no useful purpose.

TABULATION OF DATA

The analyses by the complete (fusion) method and those by the hydrochloric-acid-extraction method comprised determinations of all of the usual constituents. Those by the citric acid and water extractions were confined to the elements potassium, calcium, magnesium and phosphorus. Nitrogen (NO_3) determinations on the water extracts were made and will be included for certain purposes. In tables 1 and 1A we include all of the results of analysis by the complete and hydrochloric acid methods for purposes of record only. The discussion will be based on the figures for the more important constituents, and since the results of the citric acid and water extractions are limited to these constituents, the results by all methods are included in tables 2 and 2A.

CHEMICAL CRITERIA AND PHYSICAL TEXTURE

A basic principle in the use of chemical criteria for estimating soil fertility is that soils of the same physical texture shall be compared among themselves. Obviously no two soils are of absolutely identical physical texture and the strict application of the principle would nullify the value of any comparison. To justify the utility of such comparisons we must assume that the soils compared, if not identical in physical texture, are either so similar that they would permit of equal root dispersion or so "light" that resistance to root dispersion becomes an insignificant factor in crop production. Our five silty clay loam soils belong to an identical series and class according to the United States Bureau of Soils classification. They are therefore quite similar in physical texture, and because of the special care taken in their selection, are probably more nearly alike than an equal number of soils of the same kind taken in the course of a soil survey. If there is any validity in the physical classification, the chemical criteria should be strictly comparable among themselves. The fine sandy loams belong to an identical class, but are from different series of the United States Bureau of Soils classification. These soils, however, are of a kind in which resistance to root dispersion is unquestionably low. Their chemical characteristics are therefore logically comparable.

TABLE 1

Complete analyses of soils (fusion method)

SOIL NUMBER	SERIES	CLASS	SiO_2	K_2O	Na_2O	CaO	MgO	Mn_3O_4	Fe_2O_3	Al_2O_3	P_2O_5	SO_3	VOLATILE	TOTAL
			per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1	Yolo	Silty clay loam	60.81	1.77	1.66	1.51	4.53	0.38	7.12	14.03	0.17	0.09	8.05	100.12
2	Yolo	Silty clay loam	61.73	1.70	1.88	1.43	3.69	0.60	7.12	14.77	0.19	0.10	6.97	100.18
3	Yolo	Silty clay loam	60.45	1.85	2.07	1.50	3.57	0.41	7.32	14.15	0.21	0.05	8.43	100.01
4	Yolo	Silty clay loam	65.10	1.58	2.24	1.46	2.79	0.37	5.60	13.93	0.19	0.06	6.42	99.74
5	Yolo	Silty clay loam	65.29	1.98	2.74	1.48	2.66	0.36	5.36	13.41	0.22	0.06	6.31	99.87
6*	Yolo	Silty clay loam	61.02	1.88	2.16	1.90	3.03	0.38	7.76	14.19	0.17	0.06	7.91	100.46
7	Hanford	Fine sandy loam	62.04	2.54	2.76	3.92	2.53	0.46	5.84	15.63	0.24	0.03	3.55	99.54
8	Fresno	Fine sandy loam	68.46	2.92	3.40	3.19	1.04	0.40	4.16	14.60	0.15	0.03	1.87	100.22
9	Kimball	Fine sandy loam	66.28	3.34	2.62	2.35	1.54	0.43	6.40	14.38	0.19	0.03	3.02	100.58
10	Tejunga	Fine sandy loam	57.69	2.60	3.14	4.17	2.61	0.56	6.80	16.73	0.30	0.08	5.24	99.92
11	Madera	Fine sandy loam	56.95	1.84	2.68	4.53	3.79	0.42	7.44	16.85		0.04	5.04	99.58
12	Arnold	Fine sandy loam	64.16	2.60	3.64	3.81	1.34	0.44	4.64	16.21	0.20	0.02	2.89	99.95
13	Unclassified	Fine sandy loam	94.23	0.08	0.10	0.06	0.12	0.07	0.40	1.34	0.02	0.04	3.22	99.68
14	Standish	Fine sandy loam	58.61	1.60	2.70	4.12	1.67	0.50	6.08	18.29	0.22	0.05	5.46	99.30

* Clay loam.

TABLE 1A

Analyses by hydrochloric-acid extraction

SOIL NUMBER	SERIES	CLASS	INSOLUBLE	K_2O	Na_2O	CaO	MgO	Mn_3O_4	Fe_2O_3	Al_2O_3	P_2O_5	SO_3	VOLATILE	TOTAL
			per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
1	Yolo	Silty clay loam	70.64	0.82	0.22	1.36	3.59	0.32	7.04	9.34	0.17	0.06	6.97	100.53
2	Yolo	Silty clay loam	71.96	0.89	0.19	1.30	3.01	0.35	6.92	9.43	0.19	0.05	6.21	100.50
3	Yolo	Silty clay loam	70.49	0.89	0.21	1.48	3.32	0.35	6.96	8.84	0.20	0.05	7.17	99.96
4	Yolo	Silty clay loam	75.91	1.01	0.14	1.44	2.56	0.25	5.24	8.47	0.17	0.06	5.42	100.67
5	Yolo	Silty clay loam	75.69	1.05	0.19	1.43	2.46	0.25	5.00	7.77	0.22	0.06	6.07	100.19
6*	Yolo	Silty clay loam	70.81	0.81	0.17	1.86	2.72	0.32	7.70	9.39	0.16	0.04	6.52	100.50
7	Hanford	Fine sandy loam	79.94	0.81	0.26	2.08	1.84	0.32	5.60	6.03	0.18	0.03	3.09	100.18
8	Fresno	Fine sandy loam	90.18	0.31	0.11	1.30	0.86	0.27	3.00	2.44	0.11	0.03	1.90	100.51
9	Kimball	Fine sandy loam	83.10	0.67	0.17	1.71	1.03	0.22	6.32	4.67	0.19	0.03	2.29	100.40
10	Tejunga	Fine sandy loam	74.54	0.95	0.22	3.05	2.47	0.42	6.48	7.32	0.30	0.04	4.04	99.83
11	Madera	Fine sandy loam	75.86	0.80	0.15	2.23	2.60	0.17	6.08	8.05	0.18	0.04	3.59	99.75
12	Arnold	Fine sandy loam	85.66	0.49	0.13	0.56	0.96	0.07	4.08	5.78	0.20	0.02	2.00	99.97
13	Unclassified	Fine sandy loam	96.23	0.07	0.02	0.02	0.05	0.04	0.28	0.89	0.02	0.04	2.10	99.76
14	Standish	Fine sandy loam	75.28	0.74	0.18	2.44	1.07	0.41	5.12	9.92	0.11	0.05	4.27	99.38

* Clay loam.

TABLE 2

Silty clay loam soils of the same class and series. Arranged in order of crop (barley) producing power*

SOIL NUMBER	PRODUCTIVITY		COMPLETE ANALYSES				ACID EXTRACTIONS (HCl 1.115)				CITRIC ACID EXTRACTIONS (1 per cent)				SEASONAL AVERAGES OF H_2O EXTRACTIONS				
	General	Bushels per acre	K_2O	CaO	MgO	P_2O_5	K_2O	CaO	MgO	P_2O_5	K_2O	CaO	MgO	P_2O_5	K_2O	CaO	MgO	P_2O_5	NO_3.
			per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*p.p.m.*	†*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
5	Good	88.4	1.98	1.48	2.66	0.23	1.05	1.43	2.46	0.22	0.039	0.452	0.220	0.101	57	127	40	12	146
1	Good	86.5	1.77	1.51	4.53	0.17	0.82	1.36	3.49	0.17	0.042	0.325	0.325	0.055	48	48	38	5	131
6*	Good	85.9	1.88	1.90	3.03	0.17	0.81	1.86	2.72	0.16	0.039	0.364	0.263	0.047	40	66	35	5	141
2	Good	84.0	1.70	1.43	3.69	0.19	0.89	1.30	3.01	0.19	0.041	0.336	0.164	0.069	66	52	25	3	120
4	Medium	70.4	1.58	1.46	2.79	0.19	1.01	1.44	2.56	0.17	0.034	0.450	0.224	0.051	54	118	43	7	141
3	Poor	56.2	1.85	1.50	3.57	0.21	0.89	1.48	3.32	0.20	0.039	0.422	0.144	0.072	52	45	23	5	88
Average composition			1.78	1.48	3.45	0.20	0.93	1.40	2.97	0.19	0.039	0.397	0.215	0.070	55	78	34	6	125
Variation (per cent)			6	2	16	8	8	4	12	8	4	14	22	20	8	46	24	40	14
Maximum individual variation (per cent)			11	3	31	15	13	7	18	16	13	18	51	44	20	63	32	100	29

* Soil 6 (clay loam) is not included in the computations of averages and variations. It is placed in the table because of its general similarity, both physically and chemically, to the silty clay loams.

† p.p.m. = parts per million.

TABLE 2A

Fine sandy loam soils of the same class but different series. Arranged in order of crop (barley) producing power

SOIL NUMBER	PRODUCTIVITY		COMPLETE ANALYSES				ACID EXTRACTIONS (HCl 1.115)				CITRIC ACID EXTRACTIONS (1 per cent)				SEASONAL AVERAGES OF H_2O EXTRACTIONS†				
	General	Bushels per acre	K_2O	CaO	MgO	P_2O_5	K_2O	CaO	MgO	P_2O_5	K_2O	CaO	MgO	P_2O_5	K_2O	CaO	MgO	P_2O_5	NO_3
			per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*p.p.m.*	‡ *p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
8	Good	87.0	2.92	3.19	1.04	0.15	0.31	1.30	0.86	0.11	0.036	0.155	0.045	0.078	59	92	25	11	180
14	Good	80.8	1.60	4.12	1.67	0.22	0.74	2.44	1.07	0.11	0.036	0.264	0.104	0.040	63	71	28	9	96
11	Good	80.1	1.84	4.53	3.79	0.18	0.80	2.23	2.60	0.18	0.034	0.231	0.089	0.072	81	71	22	20	154
10	Medium	70.6	2.60	4.17	2.61	0.30	0.95	3.05	2.47	0.30	0.019	0.411	0.041	0.086	59	73	18	7	130
7	Medium	69.4	2.54	3.92	2.53	0.24	0.81	2.08	1.84	0.18	0.029	0.273	0.054	0.084	37	85	22	5	118
12	Poor	50.0	2.60	3.81	1.34	0.20	0.49	0.56	0.96	0.20	0.031	0.203	0.055	0.095	36	57	15	9	83
9	Poor	45.8	3.34	2.35	1.54	0.19	0.67	1.71	1.03	0.19	0.034	0.255	0.040	0.079	23	62	15	4	54
13*	Negligible		0.08	0.06	0.12	0.02	0.07	0.02	0.05	0.02	0.012	0.011	0.018	0.003	25	52	126	2	0
Average composition			2.49	3.73	2.07	0.21	0.68	1.91	1.55	0.18	0.031	0.256	0.061	0.076	51	73	21	9	116
Variation (per cent)			12	14	38	18	24	32	42	22	14	20	32	16	32	12	20	38	28
Maximum individual variation (per cent)			36	37	83	43	54	70	68	67	39	61	70	47	60	26	33	122	55

* Soil 13 is not included in computations of averages and variations. Its physical texture justifies classification as a fine sandy loam, but its obvious peculiarities and negligible yield make it undesirable to consider it in a determination of the characteristics of the class.

† In Soil 13 the water extractions constitute a single set of determinations.

Determination of the seasonal averages was unnecessary because of the low range observed and the lack of success in growing a crop

‡ p.p.m. = parts per million.

CHEMICAL ANALYSIS AND PRESENT PRODUCTION

If crop growth is dependent upon the ability of the soil to maintain the concentration of individual ions in the soil solution (1, 2), it would seem that any rational method should tend to show lower figures in soils of low production than in the better soils. The number of instances in which the poorer of a group of soils give lower results by any method than those from the better soils may be used as a rough measure of the rationality of the method. This, of course, is strictly true only in case all of the important soil constituents are included. None of the methods used, with the exception of the water extraction method, takes cognizance of the nitrate content of the soil. This being the case, the other methods must justify their use in soil fertility studies on the basis of the remaining constituents.

We have observed in our studies of periodic water extractions that a rise in nitrate content of a given soil is invariably attended by a rise of basic constituents and notably calcium, pointing to a close relationship between biological activities and the solutes found. In water extractions, the non-nitrate mineral constituents thus become of increased importance as an index of biological activity. No such advantage accrues to the other methods since the intensity of action of the reagents doubtless obscures the effects of organisms.

In tables 2 and 2a we have indicated by bold-faced figures those instances in which a given constituent of the poor or medium soils is lower than the same constituent in all of the good soils of the same group. The apparent deficiencies of both groups may be combined and summarized[1] in two ways.

First: Instances in which the poor and medium soils show lower figures than all of the good soils of their respective groups:

	K_2O	CaO	MgO	P_2O_5	TOTAL (EXCLUDING NO_3)	NO_3	TOTAL (INCLUDING NO_3)
Complete	1	1	0	0	2		2
Hydrochloric extraction	0	1	0	0	1		1
Citric extraction	4	0	3	0	7		7
Water extraction	3	3	4	3	13	3	16
Possible maximum	6	6	6	6	24	6	30

Second: Instances in which the poor soils show lower figures than all of the good soils of their respective groups:

	K_2O	CaO	MgO	P_2O_5	TOTAL (EXCLUDING NO_3)	NO_3	TOTAL (INCLUDING NO_3)
Complete	0	1	0	0	1		1
Hydrochloric extraction	0	1	0	0	1		1
Citric extraction	1	0	2	0	3		3
Water extraction	2	3	3	1	9	3	12
Possible maximum	3	3	3	3	12	3	15

[1] Soils 6 and 13 are not included in the summaries, although their inclusion would not change the conclusions fairly deducible therefrom.

The persistence with which low figures appear in water extractions of poor soils cannot be regarded as without significance. The same is true to a lesser degree of the citric-acid extractions, but certainly little can be said in favor of the use of either of the other methods for appraising the crop-producing power of soils.

We have purposely eliminated soil 13 from these comparisons for the reason that each and every constituent by the first three methods is very much below the same constituent in even the poorest of the other soils. All of the methods show serious deficiencies of the more important constituents so that any method would point out the limitations of this soil with reference to crop production. Indeed, a determination of silica alone should be indicative of its low fertility.

The use of chemical methods which are incapable of bringing out substantial differences between soils producing at the rate of 45 to 56 bushels of barley per acre and those producing at the rate of 80 or more bushels can hardly be justified. Water extraction does bring out substantial differences between soils; differences, moreover, which are less perceptible by other methods and which furthermore seem to be in general accord with the soils' crop-producing power.

It may perhaps be urged that a study which is limited to two classes of soil cannot have very general application. If, however, the chemical characteristics of the mineral components of soils have any influence on crop production, their effects should appear in each and every soil where they are not masked by adverse physical conditions of such magnitude as to constitute a limiting factor in crop production. Where such a condition exists no chemical method is adequate.

We are well aware that the consensus of opinion among soil investigators does not countenance the use of the complete analysis of the hydrochloric-acid extraction for predicting immediate crop yields. That they are being extensively used, however, and their application to this very purpose attempted, cannot be denied. We have ventured to present our data in the hope of still further limiting their use for such purposes.

COMPLETE ANALYSIS AND CONTINUED PRODUCTION

The complete chemical analysis has been extensively advocated as a means of forecasting the continued productivity of soils. Such a test is clearly adequate in the differentiation of soils like no. 13. All experience indicates that such soils will neither produce good crops at present without extraordinary additions of fertilizers or amendments, nor be capable of long-sustained productivity. Can we, however, justify the use of the complete analysis for

classifying soils which are sufficiently well supplied with the various important constituents to yield some crop, but nevertheless fall far below average productivity in total yield? Our soils with the exception of no. 13 represent such varying but not extreme degrees of fertility.

The complete analyses show that the poorer soils, no. 3, 9 and 12, carry totals of the same order of magnitude as the other soils of their respective groups and in spite of their comparatively low present production would be rated on an equality with the good soils by the complete analysis. All of these soils could doubtless have been brought to a high state of production by the incorporation of sufficient decomposable organic matter.[2] If the well recognized potency of organic matter in similar cases pertains to our soils, it is clear that both the present and future productivity of our poor soils is limited by the absence of an adequate nitrogen supply; or by the fact that the constituent minerals are of such a character that they will not replenish the soil solution at a sufficiently rapid rate unless they are broken down by indirect agencies such as those induced by decomposing organic matter. In either case, the limiting factor is not the totals shown by complete analysis, but the lack of absorbable forms of nitrogen or the resistant character of the constituent minerals. We take it that neither the present generation of farmers nor posterity are interested in speculations as to the relative endurance of soils which are not backed up by concrete evidence in terms of productiveness.

CHEMICAL COMPOSITION AND PHYSICAL CLASSIFICATION

Soils have from time immemorial been classified on the basis of their physical properties into such groups as clays, loams and sands. Classifications of this order have unquestionably justified their use, and, moreover, are probably in general accord with chemical composition when the soils so segregated are of the same climatic origin and environment. A question of very considerable interest is whether or not a more minute physical classification accords with differences in the chemical composition of the various groups. A comprehensive study of this question should obviously include a very large number of soils for determination of the probable variation of the various classes and individual soils within each class (5, 6). The large amount (3600 lbs.) of each soil requisite for our plot experiments necessarily limited the number of soils here reported upon. Our results, however, point to certain limitations on physical classification which may well be of extended application.

From tables 2 and 2A we have computed several sets of values, the significance of which may not be clear by inspection. "Variation" is the arithmetical mean of the individual percentage variations from the average of the group. The purpose of this figure is simply to obtain a convenient expression for measuring the extent to which the soils approach uniformity in composition. Computations of the mean probable variation by the method of least squares is of

[2] The integrity of our soils for other purposes has prevented a demonstration of this effect.

course not applicable to such a small number of soils. "Maximum individual variation" is, for each constituent, the percentage variation of that soil (highest or lowest) which deviates most from the average of all soils. Its purpose is to give an expression for measuring the extent to which individual soils deviate from the average for the group.

Soils of the same type (identical series and class)

The complete analysis may first be used as a test of uniformity in soils of the same or similar physical textures. We may then proceed to apply the figures obtained by the other methods (table 2).

The variation of the silty clay loams as shown by complete analysis is 16 per cent or less for all constituents. The maximum individual variations are of course higher. The hydrochloric-acid extraction gives results of the same order as the complete analysis as follows logically enough from the fact that the acid removes such a large proportion of the total of each ingredient. When we examine the results by the less rigorous extraction methods, differences of considerable magnitude occur. We believe that we have shown that these differences mean something in terms of crop production but they are not brought out by the physical classification. Opinion will perhaps differ as to the significance of the variations shown by complete and hydrochloric-acid extraction. It is clear, on the other hand, in view of the differences in yields of some of the soils and the great variations in the water extracts, that neither the crop-producing power of the soils nor their fertilizer needs could have been predicted from the physical classification alone.

Silty clay loam soils comprise a class of soils which represent a fairly advanced stage in the physical degradation of mineral particles. The same forces which tend to cause such changes in the size of the mineral particles are active in bringing together many different kinds of minerals. Fine soils in general are doubtless very heterogeneous in the origin of their constituent minerals, but since these consist largely of the complex silicates containing the same kinds of chemical elements, heterogeneous origin should lead to uniformity of ultimate chemical composition. Coarser soils derived from sedimentation processes might be as heterogeneous in origin and just as uniform in composition. Coarser soils "in place" would in general be derived from a more limited number of minerals and such soils from different rock formations would be likely to show greater variations in chemical composition than do the finer soils. There seems then good theoretical justification for assuming that the magnitudes of variation in the silty clay loams are at least no larger than those which would appear in the examination of other classes from the same or a different series, with the possible exception of soils of very fine texture, such as clays, which might be more uniform.

The variations found by us might have been materially lowered had we examined a very large number of soils. We do not mean to suggest that our

figures represent the probable mean variation. The individual variations, however, might and probably would have been even greater if more soils had been used.

Soils of different types (identical class but different series)

The figures (table 2A) for mean and maximum variation by complete analysis, hydrochloric and citric extraction are (with the single exception of P_2O_5 in the citric extraction) invariably higher than those shown by the Yolo silty clay loams. These differences are of considerable magnitude for most of the determinations. Apparently, then, there are greater differences, chemically as well as physically, between soils from different series of this class than between individual soils of the Yolo series of silty clay loams. To this extent the physical classification seems to be consistent, but since we have here only a single representative of each type we do not presume to offer a definite opinion on this point, nor can we extend such an opinion to terms of a generalization covering other types.

Soils of different classes

Here, again, our data are too meagre to serve as a basis for generalization. Comparison of the averages by complete analysis and hydrochloric-acid extraction shows substantial chemical differences (except in phosphoric acid) between two physical classes as here represented. It is perhaps not too much to assume that differences in ultimate chemical composition are likely to appear in comparisons of other classes. We hold, however, that chemical differences shown by complete analysis and hydrochloric acid do not determine either fertilizer needs or crop production. When we test the two classes by the figures for water extraction we see at once that the figures for a given constituent in individual soils of either class may run higher or lower than for the same constituent in individual soils of the other class. If we furthermore bear in mind that both classes include soils of good, medium and low production it is fairly obvious that physical classification into classes, as in the case of individual soils of an identical series and class, leaves much to be desired in the prediction of yields and prescription of fertilizers, however valuable it may be for determining general methods of cultivation.

CONCLUSIONS

The data presented heretofore indicate very clearly that the seasonal averages by water extraction of uncropped soils give figures more in accord with the soils' present crop-producing power than any of the usual methods. The large number of instances in which the soils of low production give low figures as compared with those obtained from soils of higher production is very striking. It is especially noteworthy that such extractions show substantial

chemical differences between soils which, on the average, vary between 50 and 80 bushels in yield. The method, therefore, is not limited to differentiation between soils of very high production and those which are totally unproductive, but may be applied to the great group of soils in which the farming population is most interested. We refer to soils so productive that the farmer cannot afford to allow them to remain uncropped, but not sufficiently productive to meet reasonable demands without fertilizers or amendments. We do not suggest that water extraction in its present development is of wide application to soils "in the field." One reason is that field soils are highly heterogeneous physically, chemically and in bacteriological flora and it is a matter of great difficulty to obtain a representative sample (8); another, that the condition of the soil at no single date is likely to represent its average condition during the growing season or at the period when temporarily depleted by plant withdrawals. W. H. Jordan in a recent paper (4) states:

> . . . . that the treatment with water gives results more significant in their relation to the productiveness of the several soils than is the case with either of the acid solutions but even with the water, if there is any significance in the results obtained, it is shown in the amounts of total soluble matter rather than in the proportions of potassium and phosphorus compounds brought into solution. Not much can be claimed, however, for a method that shows as high solubilities for a soil producing 14.1 gm. of dry matter to the box as for a soil producing 96.8 gm. of dry matter per box.

We regard Dr. Jordan's statement as generally corroborative of our conclusions. The limitation which he suggests, however, cannot vitiate our more extended conclusions, since his extractions were made on some one given date (not stated); whereas the results obtained in this laboratory are averages from results on samples taken from the plots periodically throughout the year. Since the soil comprises a dynamic system and the extracts vary in magnitude from day to day (7), its potentialities are not to be appraised on a single set of determinations.

A corollary to our conclusions as to the superiority of the water-extraction method is that all of the other methods are entirely inadequate as measures of the present crop-producing power of soils. When we come to consider criteria of soil endurance we conclude that any reagent (fusion with alkalies, strong acids, etc.) which actively attacks the soil minerals will bring out substantial differences between highly silicious soils and those containing considerable percentages of bases; but will not sufficiently distinguish between good soils and those which, while somewhat productive, will not produce average crops without additions of fertilizers or amendments. No chemical analysis is either necessary or desirable to bring out the differences between soils which approach the extremes of mineralogical composition.

The number of soil classes considered here is too limited to permit of extended generalizations as to the correlation of chemical composition of soils with their physical textures. Even if we could have shown an absolute cor-

relation between ultimate chemical composition and physical texture (6), the great variation in yields and water extracts between individual soils within a type which is probably unusually uniform, and the further fact that soils of other types belonging to a very different class frequently give figures which fall within the limits of individual variation within a type, would cast grave doubts on the adequacy of physical classification for predicting probable yields or prescribing fertilizers. It is difficult to conceive that physical classification can be applicable to any other purpose than the determination of general methods of mechanical treatment.

To be of any great value to the farmer, the physical classification must at least be supplemented by extended data as to crop history and preferably by the application of chemical and biological criteria to each individual soil. These latter must be the most important function in any adequate investigation or survey with the possible exception of those cases in which the soils examined represent great extremes of chemical composition and physical texture.

ACKNOWLEDGMENTS

The complete analyses reported herein were made by P. L. Hibbard, the hydrochloric-acid and citric-acid extractions by H. E. Billings. The mechanical analyses were made under the direction of C. F. Shaw and have been reported elsewhere for purposes of record only, no conclusions having been drawn from them (7).

The data from which the seasonal averages of the water extractions are computed were obtained by various members of the staff of this laboratory in the course of our seasonal studies. Thanks are extended to all concerned.

SUMMARY

1. Fourteen soils were studied with reference to chemical and mechanical composition and crop production under controlled conditions.

2. The soils included five individuals of a single series of one class and eight soils representing different series of another class.

3. The chemical treatment comprised complete analysis, hydrochloric-acid, citric-acid and water extractions.

4. Low figures by water extraction and to a lesser extent by citric-acid extraction are shown to be in general accord with the soils' crop-producing power.

5. Except in the case of highly silicious soils, the complete analysis and hydrochloric extractions are held to be worthless as criteria of present production or probable endurance.

6. Individual soils of a given series and class show less variation in chemical composition than do the representatives of different series of another physical class.

7. The great variation in crop yield and in the figures for water extractions, within a given series and class (soil type) indicates that physical classification into types is inadequate as a means of predicting probable yields or determining fertilizer requirements.

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